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Vegetable Oil As Diesel Fuel

Seminar III



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PREFACE

Vegetable seed oils have about 90 percent of the heat content of diesel fuel, and they have favorable energy output/input ratios of about 2 to 4:1 for unirrigated production. Current prices of vegetable oils are now more nearly competitive with petroleum prices compared with those of the recent past. Vegetable oils are readily available and are, in fact, in surplus. However, the record 1.7 billion pounds (221 million gallons) of soybean oil carryover from 1980/81 to the 1981/82 crop year represent only a small percentage (6.7 pct) of the 3.3 billion gallons of diesel oil consumed on the farm in 1978. If vegetable oil is to be considered seriously as a continuing energy crop, then an oilseed having higher productivity and oil content than soybean must be produced. Nevertheless, valid technologies must be developed for the use of vegetable oils as an alternative diesel fuel that will permit crop production to proceed in emergency situations.

Vegetable oils from seeds--such as soybean, sunflower, peanuts, rape, and coconut--are being evaluated in many parts of the world as fuel for compression ignition engines. Short-term tests were encouraging; however, long-term tests revealed problems generally attributable to inefficient combustion. This observation is especially true for direct-injection engines. At least partially responsible for the poor combustion of neat vegetable oils are their high viscosity and nonvolatility. Techniques to modify these properties are currently under investigation. New knowledge gained from continued research should provide the basis for establishing an enduring technology. Development of vegetable oils as alternative fuels for diesel engines requires input from those of many scientific disciplines. Exchange of information in the spirit of coordination and cooperation are the cornerstone to the solution of such a multi-faceted problem.

The United States Department of Agriculture, Northern Agricultural Energy Center (NAEC), sponsored Vegetable Oil as Diesel Fuel Seminars I and II in 1980 and 1981. Proceedings were arranged by extension engineers assigned to NAEC and were contracted for by Extension Service with Purdue University and the University of California. These Seminars brought into focus research on vegetable oil as fuel for compression ignition engines. Seminar I identified the need to

- establish unequivocally the chemical and physical properties of fuel constituents under investigation
- specify the extent of vegetable oil refining required
- document the test engine design features
- conduct long-term engine tests under standard, reproducible conditions
- coordinate the research efforts of various groups
- develop on-farm technology for processing and determining the economics for scale of size.

Seminar II reaffirmed some of these observations, provided some answers to previous questions, and focused attention on additional researchable problems such as the need to

- understand fuel combustion characteristics
- improve fuel combustion
- control or eliminate crankcase lubrication problems
- modify physical properties of fuels to depress the cloud point temperature.

In 1982, the American Society of Agricultural Engineers (ASAE) sponsored the International Conference of Plant and Vegetable Oils as Fuels, Fargo, N. Dak. That more formal program provided for an extensive coverage, including

- oilseed production
- fuel preparation/specifications for plant and vegetable oils
- fuel preparation/specifications for modified plant and vegetable oils
- economics of plant and vegetable oils for fuel
- engine tests with modified plant and vegetable oils
- fuel additives/thermal polymerization
- oilseed presses and extraction
- short-term engine performance
- long-term durability tests.

During the 1982 ASAE conference, NAEC was urged to provide a forum for continued vegetable oil discussions. This proceedings provides the essence of the discussions for NAEC Vegetable Oil as Diesel Fuel -- Seminar III, October 19-20, 1983, Peoria, Ill.

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CONTENTS

FUEL SOURCES--BIOMASS

Scheme of the origin and synthesis of petroleum	
M. Chang and G. T. Tsao	1
Fuels and oxychemicals through indirect liquefaction of biomass	
E. J. Soltes	5
Diesel fuels from biomass via indirect liquefaction	
J. L. Kuester	11
Seed oil crops assessment of potential oil-bearing Montana plants	
G. S. Hammaker, M. L. Marino, C. E. Simons, P. O. Kresge, and S. J. Harvey	15

FUEL SOURCES--SEED OILS

Buffalo gourd as a source of diesel fuel and ethanol on arid lands:	
Preliminary economic analysis	
L. J. Icerman and E. B. Shultz, Jr.	21
Chinese tallow tree as a diesel fuel source	
E. B. Shultz, Jr., and H. W. Scheld	25
Progress in domestication of the Chinese tallow tree <i>Sapium sebiferum</i>	
H. W. Scheld, G. N. Cameron, J. R. Cowles, C. R. Engler, A. D. Krikorian, L. J. Lester, and E. B. Shultz, Jr.	31
Fuels from thermal decomposition of vegetable oils	
G. J. Dykstra and S. C. Sorenson	38

ECONOMICS

Economics of using diverted acres to produce sunflower oil for fuel	
R. G. Johnson and A. Swenson	45
Production of oilseed crops and vegetable oil for fuel in the Pacific Northwest	
R. V. Withers, S. M. Smith, and C. S. McIntosh	51

PROCESSING AND STORAGE

Stability studies on methyl and ethyl fatty esters of sunflower seed oil	
L. M. du Plessis and J. B. M. de Villiers	57
Effect of water quality on degumming and stability of soybean oil	
H. A. M. Al-Kahtani, M. A. Hanna, and A. P. Handel	63

FUEL MODIFICATION

Partial interesterification of plant oils	
C. R. Engler, L. A. Johnson, H. Jegasothy, M. B. Reddy, and C. M. Yarbrough	71

Chemically modified vegetable oil as a diesel fuel	
D. J. Hassett	72
Esters from rapeseed oil as diesel fuel	
M. J. Nye and P. H. Southwell	78
Commercialization of ester-based diesel fuel from vegetable oils	
M. D. Webster and S. S. Fine	84
Vegetable oil methanol systems as fuels for diesel engines	
A. W. Schwab and E. H. Pryde	85
Cooperative work on engine evaluation of hybrid fuels	
E. H. Pryde and A. W. Schwab	90

FUEL PROPERTIES

Preliminary specification--Vegetable oil fuel for diesel engines	
T. W. Ryan, III	96
Effects of structure of fatty acid esters on efficiencies as diesel fuels	
W. E. Klopfenstein and H. S. Walker	102
Relationship between cetane number and structure for fatty acid esters	
W. E. Klopfenstein	104

EMA SCREENING TESTS

Alternative fuels for direct injection diesel engines	
M. Z. Ziejewski, K. R. Kaufman, and G. L. Pratt	106
Peanut oil as an emergency farm diesel fuel	
J. W. Goodrum	112
Methyl, ethyl, and butyl soybean esters as a renewable fuel for diesel engines	
S. J. Clark, L. Wagner, M. D. Schrock, and P. G. Piennaar	119
Performance and durability effects of some hybrid fuels	
C. E. Goering and B. Fry	125

ENGINE TESTS--MISCELLANEOUS

Rapid ignition quality testing	
R. R. M. Johnston and K. J. Harrington	130
Engine evaluations of linseed oil and derivatives	
G. R. Quick, P. J. Woodmore, and B. T. Wilson	138
Long-range engine tests using canola oil as a fuel	
R. C. Strayer and W. K. Craig	139
Soybean ester as alternative diesel fuel tested in DI engine-powered Volkswagen trucks	
G. H. Pischinger, A. M. Falcon, and R. W. Siekmann	145

EMISSIONS AND LUBRICATING-OIL PROBLEMS

Nonregulated exhaust emissions of Volkswagen's IDI engine fueled with transesterified or refined soybean oil either straight or blended into gasoil	
R. W. Siekmann, G. H. Pischinger, and H. Joseph, Jr.	153

Single-cylinder diesel engine study of raw and transesterified vegetable oils	
S. M. Geyer, M. J. Jacobus, and S. S. Lestz	157
Evaluation of lubricating oil contaminated with small amounts of soybean oil ester in comparison with normal diesel oil operation	
R. W. Siekmann and G. H. Pischinger	163
Performance of lubricating oils in vegetable oil/ester fueled diesel engines	
J. H. Blackburn, R. Pinchin, J. I. T. Nobre, B. A. L. Crichton, and H. W. Cruse	169
Seminar reflections and future research needs	
M. O. Bagby	171

FUEL SOURCES--BIOMASS

SCHEME OF THE ORIGIN AND SYNTHESIS OF PETROLEUM

M. Chang and G. T. Tsao ^{1/}

LONG ABSTRACT

Petroleum formation through the conversion of organic matter into hydrocarbons as catalyzed by clay had been proposed for some time. An objection to this theory arose when it was realized that envelopes of water entrapped the clay particles in their natural state. The water was thought to impair the catalytic action. In a recent study of the conversion of ethanol to gasoline, we found that water actually promoted the conversion over a synthetic aluminum silicate catalyst, ZSM-5. Whether such promotion is applicable to the clay, a natural aluminum silicate, will be an important issue in petroleum genesis.

To study this problem, we pumped a 78 percent ethanol-water solution through a micro-column reactor packed with either acidified kaolin or Fuller's earth heated to 400°C. At one atmospheric pressure, only quantitative dehydration to olefin was observed. At 1000 psi, tiny droplets of oil were formed but never separated into distinct layers. At 2000 psi, a distinct layer of slightly fluorescent, pale-yellow oil formed over the water layer.

Elementary analysis of these oil samples indicated that they were all pure hydrocarbons with hydrogen/carbon ratios of about 2. The gas chromatograms of these oils and of the lighter half of a crude petroleum are essentially identical.

Lactic acid and water mixtures were also converted to oil-like substances over the natural catalysts. The gas chromatograms showed a very broad spectrum of molecular distribution. However, a considerable number of ketones were co-generated. There was also some heavy charring that deactivated the catalysts. Elementary analysis indicated that there was about 13 percent oxygen in the oil and that the H/C ratio was around 1.5. Nevertheless, the significance of the experiment is that a substantial amount of pure hydrocarbon can be produced by the action of clay on this most common fermentation product, lactic acid.

Our current observations demonstrated that the catalytic function of the natural aluminum silicate is not impaired by the water and that the generation of petroleum-type hydrocarbons is possible through anaerobic fermentation coupled with a chemical conversion catalyzed by clay. Since the fermentation

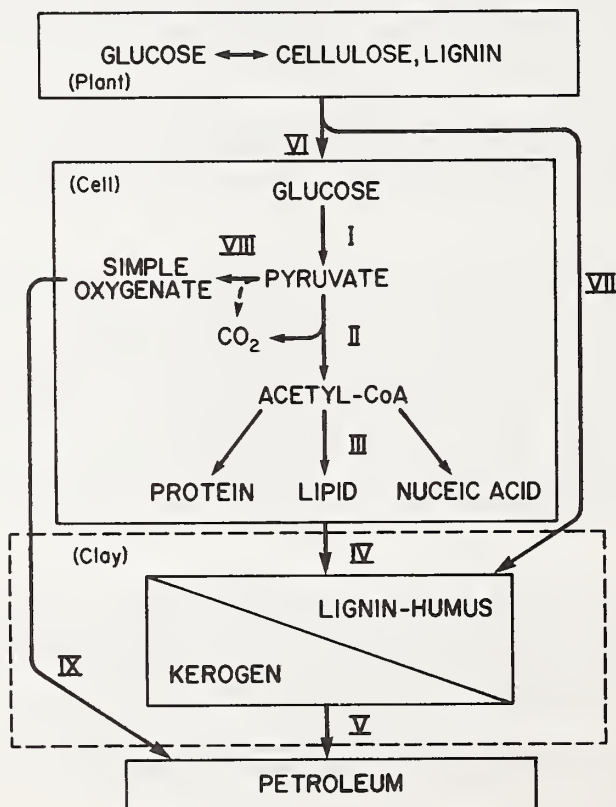
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products are primarily derived from glucose, our observations provide a direct linkage between petroleum and the sugar. A revision of the picture of petroleum genesis may be appropriate at this time.

Our literature survey revealed that, among the prominent theories of petroleum formation, two schools of thought have prevailed. The major school depicts lipids as the progenitor of petroleum. The minor school favors cellulose. Considering the fact that lipids and cellulose are both ultimately derived from glucose, a comprehensive picture of petroleum genesis using glucose as the common origin will unite these two schools of thought.

In the area of material evidence, petroleum-type hydrocarbons had been directly generated under simulated conditions from such substances as stearic acid, oleic acid, behemic acid, terpenoid, carotene, cholesterol, phytol, octyl alcohol, protein, amino acid, butanol, and acetone, etc. And we are able to add ethanol and lactic acid to the list. These substances are either the biological metabolic products derived from glucose or the anaerobic fermentation products of the sugar. It would only be logical to assume the sugar as the single most important precursor of petroleum.

A schematic representation of this comprehensive genetic picture is shown in the diagram. Glycolysis (reaction I), decarboxylation (II), and fatty acid synthesis (III) are the well-known metabolic pathways that produce lipids from glucose. Reactions IV and V represent the genetic pathway of the major school of thought, and reactions VI, and then IV and V, describe those of the



minor school. Reaction VII represents the chemical transition of carbohydrates to humus material and kerogen. Reaction IV represents the gradual transition from lignin-humus to kerogen, corresponding to the "diagenesis" in geochemistry, and reaction V may be equivalent to "catagenesis."

A third pathway may be added into the genetic picture. That is, the anaerobic fermentation-catalysis pathway shown in reactions VIII and IX. The fermentation breaks down the sugar into simple oxygenates, and the catalytic conversion transforms these oxygenates into petroleum. Through this pathway, glucose can be transformed into pure hydrocarbons without going through kerogen formation. The chemistry is apparently the simplest of all pathways, which makes a vigorous analysis of the reaction mechanism possible.

With a formula of $(\text{HCOH})_6$, glucose is a linear carbon molecule having an O/C ratio of 1 and an H/C ratio of 2. Theoretically, the molecule contains enough hydrogen to act as a precursor of petroleum if oxygen can be preferentially removed. Our analysis shows that first the C6 sugar molecule is split at the middle during the glycolysis; all the oxygen atoms are shifted to the broken ends and the hydrogens to the other ends, to create two C3 oxygenates (lactic acid and/or pyruvate). We shall call this specific sequence of reactions an "oxygen-shift" reaction. Second, by decarboxylation, the major portion of oxygen is removed in the form of CO_2 to give a hydrogen-rich compound such as ethanol. Third, dehydration then removes the last oxygen and generates C2 olefin. And, finally, polymerization produces petroleum-type hydrocarbons. Thus, through a sequence of four basic reactions, oxygen-shift, decarboxylation, dehydration and polymerization, the oxygen-loaded molecule of glucose can be converted to a spectrum of oxygen-free hydrocarbons. The first two reactions are actually completed inside the microbial cell known as the anaerobic fermentation. The last two reactions can also take place co-currently and can be catalyzed by clay. The Brownsted acid-induced polymerization inherently produces a spectrum of molecules typical of petroleum-type hydrocarbons.

With this understanding, we then proceeded to analyze the chemistry of the aerobic or lipid pathways. To our surprise, we found that all four basic chemical reactions occur during lipid formation inside the live cell. Thus, oxygen-shift and decarboxylation of glucose are completed in the initial stages of the aerobic metabolism (reactions I and II) to give the two-carbon acetyl-CoA. Through fatty acid synthesis (reaction III), the oxygen atom in the acetyl group is removed in the form of H_2O (i.e., dehydration), and the remaining C2 units are joined together (polymerization) to produce the aliphatic chain of the fatty acid. From the chemical point of view, the fatty acid can be regarded as a pure hydrocarbon except for the terminal acid group. To change the fatty acid into petroleum, all that is needed would be a simple and mild decarboxylation. Nevertheless, nature took millions of years to do just this, and the yield was about one carbon atom out of every 10,000. The natural process was, indeed, not a very efficient process.

To synthesize petroleum-type hydrocarbons from glucose, anaerobic fermentation will give a near quantitative yield of alcohol. The reaction time may range from a few days to a few hours. Equipment and technology for the fermentation are all available from existing industry. For the conversion of alcohols to hydrocarbons, industrial-grade catalysts (ZSM-5, Silicalite) are available to produce some specific petroleum products, such as gasoline. Based on our

estimation, it takes about 22 pounds of fermentation sugar to make an equivalent gallon of gasoline. Currently, the drawback of this approach is the high production cost of the fermentable sugar.

Synthetic petroleum can also be produced from vegetable oil and fatty acids by means of mild catalysis. When industrial-grade catalysts are used, the products are largely gasoline-range hydrocarbons. Technical modification to extend the boiling range of the product is possible. Presently, the most inexpensive vegetable oil in the market is a crude tall oil (about 7 cents/pound). Assuming that 80 percent conversion was possible, it would take about 10 pounds of oil to make one equivalent gallon of liquid fuel. The processing cost for a similar system was estimated at approximately 5 cents/gallon gasoline. This example illustrates the economical potential of liquid fuel production from biomass.

The origin and evolution of petroleum are further illustrated with the help of an extended Van Krevlen diagram (an H/C vs O/C plot of related materials). First, it is unambiguously obvious that glucose should be the natural precursor of petroleum. Second, the evolution from glucose to petroleum is, basically, a process of deoxygenation, and there are many ways of achieving such a process (dehydration, decarboxylation, and metabolism). Third, the conventional pathway of petroleum formation, through lignin-humus and kerogen, is essentially an inefficient dehydration pathway. Fourth, the most straightforward pathway would be the aerobic metabolism, which creates fatty acid from glucose. Fifth, through anaerobic fermentation, the glucose can be decarboxylated to alcohol and then dehydration would yield olefins. From these, catalytic polymerization will complete the final conversion to long chain hydrocarbons. It is also clear from the diagram that fatty acid is already very close to petroleum. Accordingly, a straightforward dehydration treatment might be sufficient to effect the transformation. It would also be possible to produce diesel-range hydrocarbons preferentially if one could successfully select relatively mild reaction conditions.

FUELS AND OXYCHEMICALS THROUGH INDIRECT LIQUEFACTION OF BIOMASS

E. J. Soltes ^{1/}

ABSTRACT

Catalytic hydroprocessing (hydrotreating and hydrocracking) of biomass thermochemical tars can yield mixtures of liquid hydrocarbons and alkyl aromatics of chemical compositions similar to those presently used in diesel and gasoline engine fuels. Phenolics can be co-produced. Compositions of hydroprocessed tars are similar regardless of biomass feedstock used, suggesting that the two-stage process of pyrolysis and hydroprocessing may afford a somewhat universal route to the generation of useful hydrocarbons and oxychemicals from a variety of agricultural and forestry residues.

INTRODUCTION

Thermochemical processing (gasification and pyrolysis) can accept a wide variety of biomass residue feedstocks, even dirty residues not amenable to chemical or biochemical processing, to yield gases, tars, and chars that can be used for fuels. Biomass gasification may serve gaseous fuel needs for stationary engine applications and is well suited for local energy needs (Soltes, LePori, and Pollock 1982). Gas produced via biomass gasification can also be used in Fischer-Tropsch synthesis of paraffinic diesel hydrocarbons, or following reforming, gasoline (Kuester 1983). Alternately, biomass residues can be pyrolyzed to yield tars that can be catalytically hydroprocessed into liquid hydrocarbon mixtures from which gasoline and diesel hydrocarbons can be fractionated. There are both advantages and one major disadvantage to thermochemical routes to liquid engine fuels. Advantages are that (1) residues instead of primary agricultural products can be used as feedstocks; (2) the processes are not restricted to certain types of biomass feedstocks but are flexible in their use of essentially any biomass materials; (3) the processes used are compatible with and similar to those currently used by the petroleum-processing industry; (4) both gasoline and diesel fuels are produced; (5) the products are not substitute fuels such as alcohol or seed oils but the same hydrocarbons that are currently produced and used

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in gasoline and diesel engines; and, (6) with process variations, chemicals as well as fuels can be produced. The disadvantage is that processing requirements are complex and, compared with small-scale potentials for the ethanol and seed oil options, will probably require larger scales of operation if implemented.

TAR PROCESSING

Biomass Thermochemical Tars

Depending on the pyrolysis process selected, liquid tar yield is variable but generally about 25 percent of dry feed. Tar is a complex mixture of organics. Analysis of the Tech-Air tar derived from the pyrolysis of pine bark and sawdust (Elder 1979) indicated that solvent extractable phenolics comprise approximately 13 percent of the tar in which phenol, cresol, guaiacol, dimethyl phenols, alkyl guaiacols, and eugenol are the major components. Non-extractable, high-molecular weight phenolics account for another 20 percent of the tar. Tar also contains volatile organic acids that are responsible for its corrosivity (Lin 1978), as well as a variety of neutral components (Soltes and Elder 1981).

Although reported attempts at tar utilization usually relate to direct combustion, tar is a poor liquid boiler fuel and a still poorer internal combustion engine fuel. It is viscous, gummy, not completely volatile, corrosive, exhibits high oxygen contents, and does not mix with conventional fuels. In order to use tar as an engine fuel, tar must be processed to reduce viscosity and gumming tendencies, improve volatility, remove acidity, and lower oxygen content. As most of the undesirable properties are related to high-molecular weight components and hydrophilicity, catalytic hydrocracking and hydrotreating were proposed.

Catalysts

Several types of catalysts were screened for hydrotreating and hydrotreating activity. Encouraged by the preliminary investigations with 0.5 Pt and Pd catalysts, a series of experiments was conducted with higher concentrations of noble metals on various supports. Use of these resulted in many improvements. There was more hydrogen uptake in the production of water (more oxygen removal), in the breakage of C-O bonds (removal of phenolic hydroxyl and methoxyl substituents, some cracking and reduction of acidity), in the removal of unsaturation (leading to products of light color), and in hydrocracking (higher yields of liquid product with lower viscosities). A number of these catalysts produced essentially the same results (Soltes 1983).

Hydrogen-Donor Solvents

Tetralin and decalin work well as hydrogen-donor solvents, but exhibit boiling points in the diesel fuel range. Thus, their use prevents both their recovery and the evaluation of the hydroprocessed product, or a distillative fraction thereof, as diesel fuel. The light ends of the hydrotreated product

contain the alkyl cyclohexanes, especially methyl cyclohexane, which appear to function just as well as decalin in hydrogen-donor activity in the system. Under the catalytic reaction conditions used, the phenolic hydroxyl and methoxyl moieties of pine pyrolytic tar alkyl guaiacols are split off the ring, followed by ring saturation to produce the alkyl cyclohexanes. Under less than saturation conditions (moderation of hydrotreating and hydrogenolysis activity), phenols of a reactive nature can be co-produced.

Process Flexibility

After initial work with catalysts exhibiting specificities for converting pine waste pyrolytic tar into a mixture of paraffinic fuel hydrocarbons, the research was extended to the processing of a wider range of biomass residues. We reported initially (Soltes, Wiley, and Lin 1981) that there is some compositional similarity in the volatile fractions of pine waste pyrolytic tar and corncob gasification tar. This is not totally unexpected since thermal degradation processes cannot distinguish between the cellulose, hemicellulose, and lignin composition of wood vs corncobs. Although the physical forms of various residues are different, tars produced via thermochemical processes exhibit many similarities in chemical composition.

It should be expected that tar hydroprocessing using catalysts selected for hydrogenolysis activity for carbon-oxygen bond cleavage would eradicate any differences in methoxyl substitution, and further remove phenolic hydroxyl to yield alkyl aromatics and, under saturation conditions, alkyl cyclohexanes. We can now report that the volatiles of various hydroprocessed tar products are indeed similar in composition. Compositions of these hydroprocessed tars reflect not only the alkyl aromatics expected but also a mixture of paraffinic hydrocarbons. Tars and hydroprocessed tars studied to date include those from wood wastes, corn cobs, cotton gin trash, pecan shell, peanut shell, rice hull, and sugarcane bagasse. For all, similarities in composition suggest that thermochemical conversion of biomass, with subsequent hydroprocessing of the tars produced, may be a somewhat universal system for producing chemically similar products from physically dissimilar biomass feedstocks.

Idealized Process Flow Sheet

An idealized process flow sheet for the conversion of biomass residues to gasoline and diesel hydrocarbon fuels has been described (Soltes 1983). Biomass residues are first pyrolyzed to yield gas, tar, and char products. The gas product would probably be combusted to provide heat to dry incoming feed. Tar would be catalytically hydroprocessed to yield an oil product that would serve, when fractionated, to yield light ends (recycled for solvent purposes), a middle-cut fuel feedstock, and heavy resid (recycled for cracking). The middle-cut fuel feedstock would be further fractionated into raw gasoline and diesel, which would be blended with appropriate additives to yield gasoline and diesel fuels. The gasoline fraction would contain the alkyl aromatics, such as toluene and ethyl benzene, which are used by the petroleum industry as octane boosters.

The hydrogen content of the chars produced in biomass pyrolysis is sufficient to satisfy the hydrogen requirements of catalytic hydroprocessing and, upon further study, may be available for such use through appropriate steam-char reactions. Activated carbons could be generated as byproducts. Energy requirements for both pyrolysis and subsequent processing may be derived from the gaseous products of pyrolysis.

Fuels, however, should not be the sole products in any resource conversion process. As is the case for crude petroleum, products derived from thermochemical processes are not only fuels but mixtures of chemical entities that can either be used in chemicals synthesis or be extracted for specific chemical values. Chemical values should be exploited first before relegating the bulk of any resource to fuel status. For petroleum, much use is made of its olefin content. For biomass materials, which have significant oxygen contents by elemental analysis, appropriate chemicals to be exploited are the oxy-chemicals--chemicals containing carbon, hydrogen and oxygen. In the raw tars from gasification and pyrolysis of biomass materials and in their hydrotreated products are found such oxy-chemicals in the form of phenolics, and these phenolics are currently being evaluated for their use in adhesive formulations (Soltes and Lin 1983). Apart from the use of phenolics for adhesives, several phenolics have been promoted as octane boosters (Elliott 1981) and may additionally serve fuel interests. Thus, save for catalyst requirements, all raw material and energy needs to produce liquid hydrocarbon fuels, phenolics, and activated carbons can be supplied by a biomass feedstock.

TAR PHENOLICS FOR ADHESIVES

Phenolics from Biomass Pyrolysis

The phenolics isolated from tars are derived mainly from the lignin in lignocellulosics (Soltes, Wiley, and Lin 1981). The 4-alkyl guaiacyl (4-alkyl, 2-methoxy phenol) unit is recognized as a major building block in pine lignin, and the chemical composition of the phenolics in the Tech-Air tar from pine wastes reflects this fact. The addition of formaldehyde to phenolics to form methylol derivatives is an electrophilic substitution reaction favoring ortho- and para- positions. The blocking of these active ring sites by methoxyl and alkyl groups in the alkyl guaiacols therefore makes the desired methylol derivatives difficult to prepare. However, it is still possible to use these pyrolytic oil phenolics for adhesive synthesis.

Elder (1979, Elder and Soltes 1979, 1980) examined the use of Tech-Air pine waste pyrolytic tar phenolics in formaldehyde methylolation and condensation reactions. He observed little or no reaction between water-soluble phenolics and excess formaldehyde under moderate alkaline conditions. However, if the pH of the reaction medium was adjusted to either 3 or 11, products exhibited fair adhesion properties when applied to pine veneers. The resultant veneer sandwiches were partially resistant to the cyclic boil test, a rugged test procedure designed to evaluate exterior-grade adhesives.

Parris (1982), using 4-methyl guaiacol as a model compound in methylation experiments, confirmed that the use of higher pH's can force methylol substitution reactions. Mass spectrometry and proton NMR analyses of the products indicated that at least three products were formed in the reaction. Although the addition of formaldehyde to the position meta- to the hydroxyl group was not believed probable because of the overriding ortho/para directing influence of the phenolic -OH group, the formation of these methylol products suggested that meta- addition of formaldehyde is not impossible.

Simply, if these phenolics are to be used in adhesives, methylation must be promoted. One approach is to convert these alkyl guaiacols into more reactive compounds. Guaiacol can be readily demethylated to produce catechol (o-hydroxy phenol), which provides four positions on the phenolic ring for electrophilic substitution. This number of formaldehyde-reactive sites enhances chances of forming three-dimensional polymers required in adhesive synthesis. Resorcinol (m-hydroxy phenol) is an excellent phenol for formaldehyde reactions, and the resorcinol-formaldehyde adhesive resin produced commercially has excellent bonding and durability properties. Experiments undertaken by Lin and Soltes (1983) indicate that adhesives can be successfully prepared from catechol having properties similar to that from resorcinol. The conversion of the alkyl guaiacol compounds found in pyrolytic tar to alkyl catechols for the purpose of synthesizing alkyl catechol-formaldehyde adhesives has also been undertaken. Preliminary results reveal that methylation and condensation can take place, with the adhesive products resembling the catechol-formaldehyde adhesive.

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Diesel Fuels From Biomass via Indirect Liquefaction

J. L. Kuester^{1/}

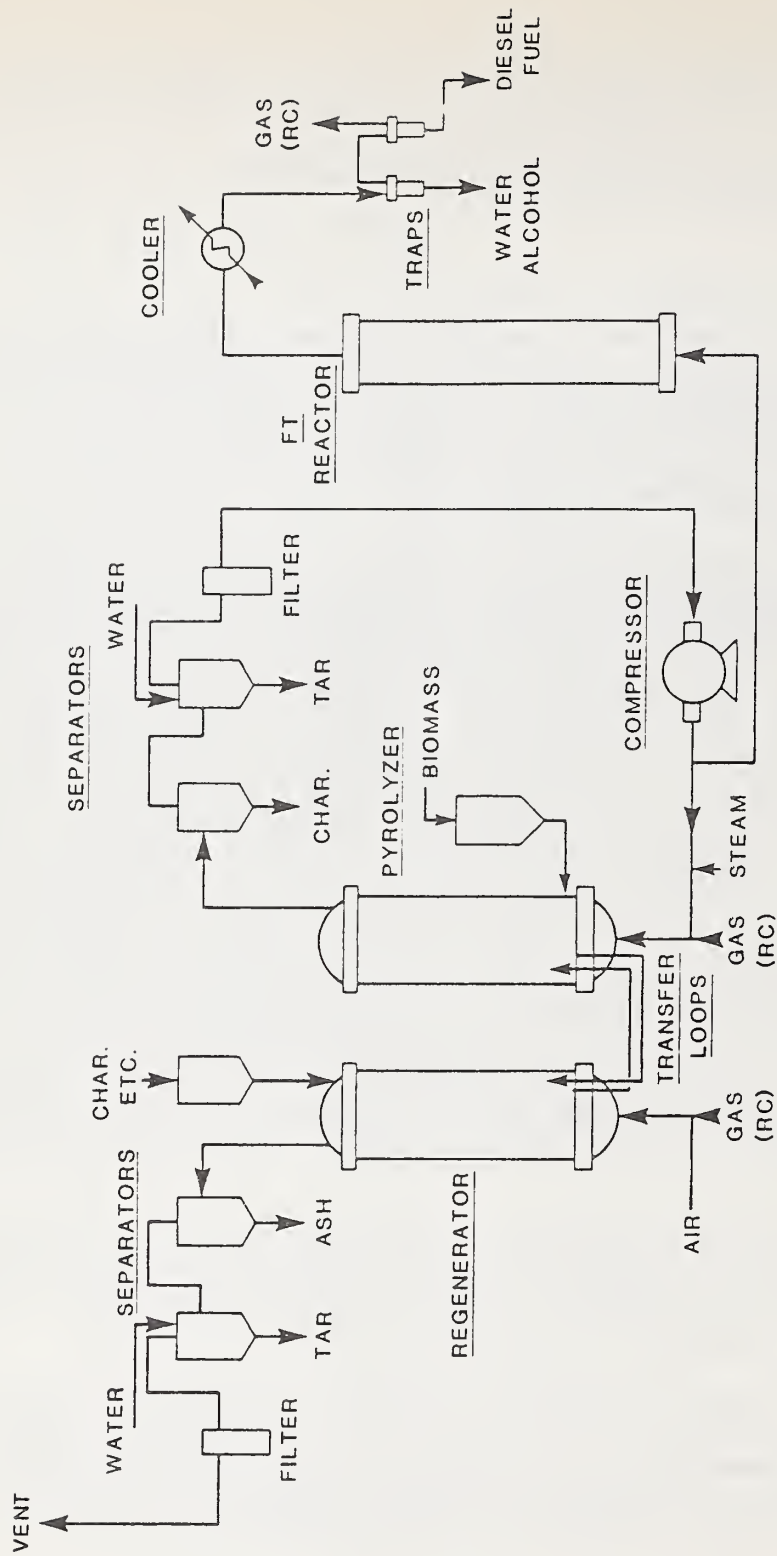
A research project to convert various biomass materials to an equivalent of a No. 2 diesel fuel is in progress at Arizona State University. The objective is to maximize diesel yields at as small a scale as is commercially viable. Ideally, the process would be portable with fuel quality compatible with transportation and industrial machinery operating in the immediate area.

A schematic of the process is shown in figure 1. Biomass feedstock (single species or mixtures) is fed continuously into a gasification system consisting of a fluidized bed pyrolyzer and regenerator. A solid (catalytic or inert) is heated in the regenerator in a standard combustion mode and continuously circulated between the two vessels. The biomass is "flashed" to a gas consisting of hydrogen, carbon monoxide, olefins, paraffins, and CO₂. A combination of steam and recycle gas from the liquefaction system is used to fluidize the pyrolyzer. Air and recycle gas is used to fluidize the regenerator. The pyrolysis gas is passed thru a cyclone and scrubber before being fed into a catalytic liquefaction reactor. Both fluidized bed and slurry phase type liquefaction reactors are under study. From the liquefaction reactor, two immiscible liquid phases are condensed: (1) water - alcohol, and (2) liquid hydrocarbon fuel. The alcohol portion is primarily normal propanol while the liquid hydrocarbons are very paraffinic (straight chained) in the C₅-C₁₇ range. Cetane indices and heating values are equivalent to those for No. 2 diesel fuel. The processing scheme allows for ease of separation of oxygenated compounds from the liquid hydrocarbons. Thus the oxygen in the biomass ends up in carbon dioxide, water and normal propanol for the overall process.

Liquid hydrocarbon fuel yields are currently in the range of 40-50 gallons per ton of feedstock (dry, ash free basis). The theoretical maximum is about 90 gals/ton. A level of about 60 gals/ton is expected to be reached at economically attractive operating conditions.

A large variety of feedstocks have been tested in the laboratory (see table 1). In general, all the feedstocks will produce a quality product. Yields will be dependent on the pyrolysis gas composition potential of the feedstocks. Some variations have been observed. Thus cork materials produce a high olefin content while Euphorbia lathyris gives a high H₂/CO ratio.

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GASIFICATION

LIQUID FUELS SYNTHESIS

Figure 1.--Conversion system schematic.

Table 1.--Feedstock list
(THE SCIENTIFIC NAME IS LOCATED UNDER THE COMMON NAME WHERE APPROPRIATE)

1) Euphorbia lathyris Euphorbia lathyris	32) Pokeweed Phytolacca americana	62) Round-leaf milkweed Asclepias spp.
2) Candellilla bagasse Euphorbia antisiphilitica	33) Tall boneset Eupatorium altissimum	63) Cotton seed meat Gossypium Thurberi
3) Raw guayule Parthenium argentatum	34) Rosin weed Silphium integrifolium	64) Cotton seed Gossypium Thurberi
4) Guayule resins Parthenium argentatum	35) Tall goldenrod Solidago altissima	65) Cotton seed lint Gossypium Thurberi
5) Guayule bagasse Parthenium argentatum	36) Sassafras Sassafras albidum	66) Cotton seed meal Gossypium Thurberi
6) Guayule cork Parthenium argentatum	37) Coral berry Symphoricarpos orbiculatus	67) Cotton seed hulls Gossypium Thurberi
7) Greasewood Sarcobatus vermiculatus	38) Wild bergamot Monarda fistulosa	68) Cotton gin trash Gossypium Thurberi
8) Jojoba meal Simmondsia chinensis	39) Russian thistle Salsola Kali	69) Skunkbush Rhus trilobata
9) Almond hulls Terminalia catappa	40) Water hyacinth Hyacinthus spp.	70) Yerba-santa Eriodictyon angustifolia
10) Almond shells Terminalia catappa	41) Common milkweed Asclepias syriaca	71) Fourwing saltbush Atriplex canescens
11) Almond prunings Terminalia catappa	42) Swamp milkweed Asclepias incarnata	72) Netleaf hackberry Celtis reticulata
12) Sugarcane bagasse Saccharum officinarum	43) Peat Sphagnum spp.	73) Catclaw mimosa Mimosa bluncifera
13) Wheat straw Triticum aestivum	44) Portuguese oak cork Quercus suber	74) Sewage sludge
14) Creosote bush Larrea tridentata	45) Silver maple Acer saccharinum	75) Corn starch
15) Fir bark Pseudotsuga menziesii	46) Yellowleaf sliktassel Garrya flavescens	76) Coal
16) Arizona cypress Cupressus arizonica	47) Sweet sorghum Sorghum saccharatum	77) Polyethylene
17) Pringle manzanita Arctostaphylos Pringlei	48) Pale Indian plantain Cacalia atriplicifolia	78) Polypropylene
18) Wright sliktassel Garrya Wrightii	49) Tall bellflower Campanula americana	79) Lignin
19) Pointleaf manzanita Arctostaphylos pungens	50) Cherry elaeagnus Elaeagnus multiflora	80) Saw dust
20) Shrub live oak Quercus turbinella	51) Grass leaved goldenrod Solidago graminifolia	81) Paper chips
21) Hairy mountain mahogany Cercocarpus breviflorus	52) Common elder Sambucus canadensis	82) Hog fuel
22) Utah juniper Juniperus osteosperma	53) Canada wildrye Elymus canadensis	83) Mesquite Prosopis torreyana
23) Pinyon pine Pinus edulis	54) Field thistle Cirsium discolor	84) Calotropis Calotropis procera
24) Velvet mesquite Prosopis juliflora var. retorta	55) Sow thistle Sonchus oleraceus	85) Rice hulls
25) ECO FUEL II (municipal preprocessed refuse)	56) Compass plant Silphium laciniatum	86) Black greasewood Sarcobatus vermiculatus
26) Raw kelp	57) Canalgre roots Rumex hymenosepalus	
27) Kelp residue	58) Cut leaf tassel Dipsacus laciniatus	
28) Smiling sumac Rhus copallina	59) Blue tassel Dipsacus sylvestris	
29) Smooth sumac Rhus glabra	60) American germander Teucrium canadense	
30) Red tatarian honeysuckle Lonicera tatarica	61) Woody milkweed Asclepias spp.	
31) Giant ragweed Ambrosia trifida		

Abbreviations:

var. = variety

spp. = species

Work on the project continues with the following major tasks:

- (1) Increase diesel fuel yields.
- (2) Assess liquefaction catalyst life/regeneration characteristics.
- (3) Explore alternative (higher valued) products with the same basic processing scheme.
- (4) Simplify the process to allow for a lower break-even scale.
- (5) Scale-up.

Current funding allows for a continuation of laboratory scale research and the design of an intermediate scale facility. The primary purpose of the intermediate scale is to produce a large quantity of product for applications testing and to assess the performance and reliability of the process with equipment sizes closer to commercial reality.

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ABSTRACT

An inventory of native and naturalized Montana species with potential as oil-bearing plants was made. Eighteen of the most promising oilseed species and twenty seven of the most promising whole-plant-oil species were selected for field sampling. Field samples were taken and analyzed for oil, protein, fiber, ash, and moisture. Carbohydrate and TDN were calculated. On the basis of the laboratory analyses and observed and published agronomic characteristics, species were ranked for further study.

INTRODUCTION

The Montana Department of Natural Resources and Conservation is conducting a Sustainable Energy Assessment (SEA) project to assess the potential for energy conservation and renewable energy within Montana. This work was the initial step in the research and identification of potential oil-bearing plants that may be cultivated in Montana. The ultimate goal of this portion of the state's SEA project is to encourage to the extent feasible the development of oil-bearing crops whose oil can be used as diesel fuel substitutes and extenders.

This research identified oil-bearing plants--both oilseed and whole-plant-oil--now grown and those that might be grown in Montana. Native and naturalized plants identified as potential oil-bearing crops, but not currently grown commercially, were sampled and tested for oil content. The most promising plants were examined for feed quality.

In conjunction with this study, research was also conducted to determine the location and amount of land in Montana that could produce oil-bearing crops. Requirements including costs for planting, cultivating, and harvesting the near-term crops were assessed, using crop budgets.

EXPERIMENTAL PROCEDURE

Inventory of Montana Oil-Bearing Plants

An inventory of currently cultivated and native and naturalized Montana oil-bearing species was developed. The locations, yields, and other characteristics for the oilseed crops now grown in Montana--sunflower,

^{1/}Work sponsored by the Montana Department of Natural Resources and Conservation under the Sustainable Energy Assessment Project.

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flax, safflower, mustards, and rapeseed were summarized. Two types of oil-bearing plants, oilseed species and whole-plant-oil species, were assessed for inclusion in the inventory. Native and naturalized species, identified as having high oil content, were evaluated for habitat constraints and agronomic problems. Species having known constraints or problems were eliminated. Most of the retained annual and perennial oilseed and whole-plant-oil species were ultimately collected and analyzed for oil content and feed components.

Plant Sampling and Testing

Potential sampling sites were selected prior to actual sampling and four major collecting trips within the area from the Rocky Mountain front (Bozeman to Shelby) east to Miles City conducted. Actual sampling sites were selected as species were located during each trip. Three sites for each species were selected when possible; fewer sites were located for some uncommon species. More sites were sampled when either few plants per site or few plants in collectable condition per site were found. For these, samples from several sites were combined to obtain a large enough sample for analysis.

Plants for collection were selected randomly. Seed (or fruit) samples were collected only from mature plants. Whole plant samples of mature plants (slightly before seed disposal) were obtained by cutting the plants at ground level. Seed and whole plant samples were further prepared at Montana State University by seed cleaning (e.g., thrashing, air separation) for seed samples and by drying and grinding for whole plant samples. The prepared samples were then shipped to Doty Laboratories, Inc., of North Kansas City, Mo., for seed and whole plant analyses.

Analyses included oil content and tests to examine feed quality, i.e., protein, carbohydrates, fiber, and total digestible nutrients. The feed quality tests were run only if the oil content was above 20 percent for the seed-oil plants and 3 percent for the whole-plant-oil plants.

RESULTS AND DISCUSSION

Results

Tables I (oilseed species) and II (whole-plant-oil species) present the analysis results.

Investigated species were next placed into priority groupings for further research. Placement was based principally on oil content, but feed quality, toxicity, and field observations on agronomic potential were considered as well.

Adaptable Oil-Bearing Plants

Promising, oil-bearing, nonnative plants were examined and their ability to adapt to Montana conditions was assessed. Plants, which have become well known for their oil-producing capabilities, as well as nonnative mustards grown previously in Montana, were investigated.

Table 1. Seed-analysis results for native and naturalized potential oilseed species retained after preliminary habitat and agronomic examination

Family	Species	Common name	Site identification number	Percentages 1/					Plant part analyzed
				Oil	Protein (Nx6.25)	Carbohydrates 2/	T.D.N. 3/	Fiber	
Asteraceae	<u>Xanthium strumarium</u>	Cocklebur, Cow Cockle	23	10.0	-	-	-	-	Seed and pericarp
Brassicaceae	<u>Brassica kaber</u>	Wild Mustard, Charlock	7, 12	18.2	-	-	-	-	Seed
	<u>Camelina microcarpa</u>	Smallseed Falseflax,	Multiple 4/ 21	24.6	27.6	43.9	126.9	17.4	Seed
		Hairy Falseflax		23.3	26.2	47.8	126.4	37.7	Seed
	<u>Sisymbrium altissimum</u>	Jim Hill Mustard, Tumble Mustard	15	28.4	34.7	33.2	131.7	7.9	Seed
	<u>S. loeselii</u>	Loesel Tumble Mustard	28	32.2	29.8	33.9	136.2	7.8	Seed
			1	27.9	29.5	39.8	131.9	14.9	Seed
	<u>Thlaspi arvense</u>	Field Pennycress, Fanweed	13	35.6	31.1	30.1	141.5	5.3	Seed
				17.7	30.3	48.7	118.6	35.2	Seed
	<u>Cleome serrulata</u>	Rocky Mountain Bee Plant, Stinkweed	11	23.3	23.5	49.8	125.7	32.3	Seed
Chenopodiaceae	<u>Kochia scoparia</u>	Kochia, Summer Cypress	1	8.2	-	-	-	-	Seed
	<u>E. marginata</u>	Snow-on-the-Mountain	24	25.6	17.6	51.7	126.9	23.5	Seed
	<u>Mentzelia decapetala</u>	Tenpetal Blazingstar, Sandy Lily	29, 30	28.5	19.0	39.0	122.1	17.3	Seed
Papaveraceae	<u>Argemone polyanthemus</u>	Prickly Poppy	18, 19, 20	36.0	17.4	41.6	140.0	11.7	Seed

1/ All data were calculated on a dry weight basis. When oil content was below 20 percent, no other tests were run.

2/ Includes fiber and nitrogen-free extract.

3/ T.D.N. = total digestible nutrients. Following procedures of Doty Laboratories, Inc., we assumed no digestibility coefficients in calculating T.D.N. (i.e., T.D.N. = 2.25 x oil (%) + carbohydrates (%) + protein (%)). Thus, this T.D.N. expresses the total potential nutrients available in the seed. See text page 56 for further explanation.

4/ Includes sites 3, 4, 7, 8, 9, and 16.

5/ No sites were located for: Asteraceae Helianthus petiolaris Prairie Sunflower
 Brassicaceae Descurainia pinnata Tansymustard
D. sophia Flixweed
Isatis tinctoria Dyer's Wood, Yellow Wood
 Euphorbiaceae Euphorbia esula Leafy Spurge
E. spathulata Spatula-leaved Spurge
 Onagraceae Gaura parviflora Small-flowered Gaura

Source: Development Planning and Research Associates, Inc.

Table 11. Plant analysis results for native and naturalized potential whole-plant-oil species retained after preliminary habitat and agronomic examination.

Family	Species	Common name	Site identification number	Percentages 1/				
				Oil	Protein (Nx6.25)	Carbohydrates 2/	T.D.N. 3/	Ash
Asclepiadaceae	<u>Asclepias speciosa</u>	Showy Milkweed	29	5.7	11.6	74.8	99.2	7.9
			39	6.1	10.5	70.9	95.1	12.5
			40	6.2	10.9	74.3	99.2	8.5
Asteraceae	<u>Achillea millefolium</u>	Yarrow	Plants not in collectable condition					
				-	-	-	-	-
				-	-	-	-	-
	<u>Artemisia campestris</u>	Field Sagewort	32	6.9	5.7	82.6	103.8	4.7
			38	5.6	5.1	83.1	100.8	6.2
	<u>A. ludoviciana</u>	Cudweed Sagewort	34	3.8	4.7	87.0	100.3	4.5
			34	5.1	13.7	74.9	100.1	6.4
			40	2.6	-	-	-	-
	<u>Carduus nutans</u>	Nusk Thistle	17	1.7	-	-	-	-
			26	3.7	9.0	75.6	92.8	11.7
			27	2.2	-	-	-	-
	<u>Chrysothamnus nauseosus</u>	Rubber Rabbitbrush	30	8.7	8.7	77.7	106.0	4.9
			31	8.0	8.1	79.6	105.7	4.4
	<u>Cirsium arvense</u>	Canada Thistle	2	2.5	-	-	-	-
			10	4.6	8.7	76.9	96.0	9.8
			28	3.4	8.8	75.6	92.1	12.2
	<u>C. undulatum</u>	Wavyleaf Thistle	32	5.5	7.4	79.2	98.9	7.9
	<u>Grindelia squarrosa</u>	Curly-cup Gumweed	32	13.1	8.2	68.6	106.3	10.1
			33	10.0	7.6	73.5	103.6	8.9
			38	10.7	12.5	67.5	104.1	9.3
	<u>Gutierrezia sarothrae</u>	Broom Snakeweed	28	7.8	7.3	66.6	91.5	18.3
			35	6.4	6.6	68.2	88.3	18.9
			41	7.6	10.6	64.9	92.6	16.9

Continued....

Table II. (Continued)

Family	Species	Common name	Site identification number	Oil	Protein (Nx6.25)	Percentages		
						Carbohydrates 2/	T.D.N. 3/	Ash
Chenopodiaceae	<u>Liatris punctata</u>	Dotted Blazingstar	35	5.3	6.2	80.0	98.0	8.5
			36	5.2	6.4	80.0	98.1	8.4
	<u>Solidago rigida</u>	Stiff Goldenrod	34	8.3	5.4	80.2	104.3	6.1
			35	8.1	6.5	79.1	103.8	6.4
			36	8.9	5.7	78.6	104.3	6.7
	<u>Tragopogon dubius</u>	Common Salsify	30	5.0	5.3	80.5	97.1	9.3
Euphorbiaceae			33	5.2	5.4	79.6	96.7	9.8
	<u>Chenopodium album</u>	Lambsquarter, White Goosefoot	Seeds already dispersed		-	-	-	-
	<u>Kochia scoparia</u>	Kochia, Summer Cypress	4	3.1	12.9	72.9	92.8	11.1
			38	3.8	12.8	73.3	94.7	10.0
			39	2.7	12.8	74.2	93.1	10.3
	<u>Salsola kali</u>	Russian Thistle	39	5.3	10.8	67.6	90.3	16.4
Gramineae			41	4.7	6.9	73.8	91.3	14.9
	<u>Euphorbia esula</u>	Leafy Spurge	2	4.9	7.6	78.3	96.9	9.2
	<u>E. marginata</u>	Snow-on-the-Mountain	24	4.7	9.7	72.7	93.0	12.9
	<u>Agropyron repens</u>	Quack Grass	27	2.2	-	-	-	-
			28	2.8	-	-	-	-
	<u>Elymus canadensis</u>	Canada Wildrye	Seeds already dispersed		-	-	-	-
Papaveraceae	<u>Argemone polyanthemus</u>	Prickly Poppy	19	1.9	-	-	-	-

1/ All data are calculated on a dry weight bases. When oil content was below 3 percent, no other tests were run.

2/ Includes fiber and nitrogen-free extract.

3/ T.D.N. = total digestible nutrients. We assumed no digestibility coefficients in calculating T.D.N. (i.e., T.D.N. = 2.25 x oil (%) + carbohydrates (%) + protein (%)). Thus, this T.D.N. expresses the total potential nutrients available in the seed. See text page 56 for further explanation.

4/ No sites were located for: Asclepiadaceae Asclepias syriaca Common Milkweed
A. verticillata Whorled Milkweed
A. viridiflora Green Milkweed
Asteraceae Chrysothamnus viscidiflorus Green Rabbitbrush
Caprifoliaceae Symphoricarpos orbiculatus Coralberry
Euphorbiaceae Euphorbia spathulata Spatula-leaved Spurge

Source: Development Planning and Research Associates, Inc.

Species with the greatest near-term potential in Montana are rapeseed (Brassica napus and B. campestris) and crambe (Crambe abyssinica). The first is already cultivated in Canada and likely could be readily adapted to Montana, especially in the more western and northern areas with cool July's. Crambe, though not commercially grown, has been shown to produce good yields in Montana, provided it is planted early in the season.

Members of the Lesquerella (bladderpod) genus may have potential in Montana, however, realization of their potential is probably much longer term than crops currently grown.

Other popularized species such as jojoba, buffalo gourd, money plant, castor, meadowfoam, gopher weed, Chinese tallow tree, and Stokes' aster have habitat constraints (e.g., growing-season length, temperature, and moisture requirements) that would make them difficult (or impossible) to adapt to cultivation in Montana.

CONCLUSIONS

Conclusions resulting from the study are

- o Twenty-two native or naturalized perennials and sixteen annuals show potential as seed oil plants.
- o Twenty-seven native or naturalized species show good potential as whole-plant-oil plants.
- o Seven native or naturalized species, prickly poppy, snow-on-the-mountain, spatula-leaved spurge, small-flowered gaura, Dyer's woad, prairie sunflower, and Jim Hill (or tumble) mustard, show high potential for seed oil. Six species, smallseed falseflax or hairy falseflax, tansymustard, flixweed, tenpital blazingstar or sand lily, loesel tumble mustard, and cocklebur or cow cockle, show medium potential.
- o Five native or naturalized species, rubber rabbitbrush, field sagewort, showy milkweed, curly-cup gumweed, and stiff goldenrod, show high potential for whole-plant oil, with rubber rabbitbrush showing the greatest potential. Five species, wavyleaf thistle, snow-on-the-mountain, broom snakeweed, Russian thistle, and common salsify, show medium potential.
- o Problems could occur with some of the promising species that are now considered weeds.
- o Crambe and rapeseed offer potential for near term cultivation in Montana.
- o Members of the Lesquerella genus (bladderpod) offer longer term potential for adaptation to cultivation in Montana.
- o The well publicized oil-bearing species, e.g. jojoba, buffalo gourd, gopher weed, money plant and castor, have habitat constraints that make them difficult or perhaps impossible to adapt to cultivation in Montana.
- o The economics of oilseed crop production compare favorably today with that of wheat and barley. However, the feasibility of producing plant oils for diesel fuel in an emergency situation will be determined by the value placed on preserving the productivity of the dependent economic segments.

FUEL SOURCES--SEED OILS

BUFFALO GOURD AS A SOURCE OF DIESEL FUEL AND ETHANOL
ON ARID LANDS: PRELIMINARY ECONOMIC ANALYSIS

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EXTENDED ABSTRACT

Buffalo gourd is native to the semi-arid southwestern United States and requires substantially less water than conventional crops grown there. It yields a seed oil that is intermediate in properties between soy and sunflower oils, as well as large starchy roots suitable for ethanol production. Cost parameters and conversion factors from published literature on buffalo gourd and southwestern crops have been used in a preliminary estimation of net annual revenue, \$137 and \$70 per acre for dryland and irrigated cases, respectively, land charges not included. On the same basis, grain sorghum and corn returned substantially less.

Background

Buffalo gourd (Cucurbita foetidissima HBK) is a member of the pumpkin-squash genus. The seeds, which account for about one-third of the weight of the hard-shelled fruit, contain 30-40 wt percent oil and 30-35 wt percent protein. Roots develop prolifically from vine nodes; four-year-old roots may weigh over 40 kg (fresh basis) and contain 50-56 wt percent starch on a dry basis.

The range of the buffalo gourd extends from the southern Great Plains southward almost to Mexico City. At least 25 Major Land Resource Areas (MLRAs)^{3/} are suitable for the buffalo gourd in the southwestern United States. Of interest are MLRAs 77 (Southern High Plains - Texas and New Mexico), 70 (Pecos-Canadian Plains and Valleys - New Mexico), 42 (Southern Desertic Basins, Plains and Mountains - New Mexico and Texas) and 78 (Central Rolling Red Plains - Texas and Oklahoma).

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^{3/} MLRAs are geographically associated land resource units or ecological zones, defined by the Soil Conservation Service of the U.S. Dept. of Agriculture (Land Resource Regions and Major Land Resource Areas of the United States, USDA Soil Conservation Service, Agriculture Handbook 296, Revised Dec. 1981).

The buffalo gourd is a drought-tolerant plant, surviving at about 40°C on as little as 6 inches of water annually. A minimum of 10 inches is probably needed to produce a crop. Yields should increase with more than 10 inches, but extended periods of excessive moisture cause root rot. A novel cropping system to optimize root starch yields and prevent overcrowding calls for alternate swaths to be dug annually to remove all roots in the swath. The next year the harvested swath would be regenerated by asexual rooting of the vines that would creep over from the unharvested swath.

Bemis and his co-workers at the University of Arizona, Tucson, have begun work on the domestication of the buffalo gourd, with emphasis on hybridization to increase oil content of the seeds up to the 40 wt percent level. Preliminary data indicate that annual yields of 3000 kg of seed per hectare (2680 lb per acre) may be possible, suggesting that about 1000 lb of oil might be produced per acre, annually. Currently, the most productive commercial oilseed in the United States in terms of annual oil yield is the peanut, which gives about 700 lb oil per acre per year in the humid Southeast. Therefore, if buffalo gourd can measure up to Bemis' estimates in the field, it might become the leading seed oil producer per acre in the United States.

The Iodine Value (IV)^{4/} of buffalo gourd oil has been reported as 129.9. This is in the typical range for soybean oil and at the low end of the typical range for high linoleic sunflower oil. Comparison of the fatty acid distributions of the three oils--buffalo gourd oil, soybean oil, and sunflower oil--indicates that they are similar in terms of chemical structure. Therefore, buffalo gourd oil should not be regarded as an exotic oil. Soybean and sunflower oils are well-known and well-tested in a multitude of uses.

Of special interest to us is the possibility that buffalo gourd might become an important economic crop in eastern New Mexico and the Texas panhandle in MLRA 77, underlain by the Ogallala aquifer. Because buffalo gourd requires much less water than conventional crops, the life of the aquifer could be effectively extended in this portion of the High Plains. Recharge to the aquifer is limited to the amount of rainfall that percolates down to the water table about two cm per year. Throughout most of the High Plains, water is being pumped out much faster than this rate. Much of the aquifer may be totally exhausted in the next 30-50 years. The cost of natural gas, the primary fuel used to pump irrigation water, has risen by more than tenfold from 1974 to 1981. As a result, even farmers with large amounts of water under their land often cannot afford to pump it to their crops. Clearly, there is a need to investigate novel crops that require little water. Study of the rainfall history in the region suggests that buffalo gourd might produce economic yields without irrigation, relying only upon annual rainfall for needed moisture. Even if irrigation has to be utilized, the plant would require smaller amounts than conventional crops.

^{4/} Iodine Value is related to the presence of double bonds (unsaturation) in a triglyceride seed oil. High values indicate that the oil may polymerize readily in the crankcase if it fails to combust and blows-by the piston rings. Pryde has urged an upper limit of 145 for satisfactory diesel performance.

Buffalo Gourd for Diesel Fuel

To the best of our knowledge, buffalo gourd oil has been tested only once in a diesel engine, for 45 minutes. Long-term testing for several hundred hours will be necessary to establish technical feasibility. However, encouragement can be taken from the chemical characteristics of buffalo gourd oil that reveal it to be similar to both soybean and sunflower oils. Both of these conventional seed oils have been successfully tested in diesel engines under long-term conditions.

Buffalo Gourd for Ethanol

Only one test has been conducted, to the best of our knowledge, on the fermentation of the starch in buffalo gourd root. The single small-scale laboratory test resulted in 52.5 percent conversion of the starch to alcohol; a yield of 245 gallons of alcohol per acre was calculated. In the same series of laboratory tests, sugar beets, corn, and grain sorghum were fermented in the same system. The alcohol yields from these comparison substrates averaged 75 percent of published large-scale yields of alcohol from the same raw materials. Therefore, if one assumes that buffalo gourd laboratory results represent 75 percent of what a large-scale optimized fermentation unit would accomplish, the average practical annual yield of alcohol can be estimated as 327 gallons per acre, equivalent to about 30 million Btu per acre per year.

If this value of 327 gallons per acre, or some value in the range of 300 to 400 gallons per acre, is supported by pilot-plant fermentation tests, it would place buffalo gourd in the top rank of ethanol crops, roughly comparable to sugar beets, somewhat lower than sweet sorghum, and well ahead of corn and grain sorghum. The leader, sugarcane, would be difficult to match at over 600 gallons per acre. However, it should be noted that sugarcane requires ample water and special growing conditions available only in limited areas of the United States, and buffalo gourd does not need such special land or much water, nor does it require the prime midwestern farmland needed by corn and other major food crops.

Economics of Buffalo Gourd in New Mexico

A preliminary economic analysis was carried out by us based on conservative estimates of product yields, variable and fixed costs of buffalo gourd farming and processing, and revenues. Average-to-high cost estimates and low-to-average conversion values were chosen. The results indicate that net revenues per acre for the production of buffalo gourd-based fuels are positive for both dryland and irrigated farming. Yields are assumed not to increase with the application of irrigation.

Net annual per acre returns of about \$137 and \$70 for dryland and irrigated production, respectively, were calculated. An alternative interpretation of this analysis is that 352 gallons of portable fuels capable of being mixed directly with diesel fuel and unleaded gasoline could be produced for \$0.99/gal (dryland) to \$1.18/gal (irrigated) without the sale of seed meal or fermentation by-products, \$0.72 gal (dryland) to \$0.91/gal (irrigated) with the sale

of seed meal at \$0.07/lb, or \$0.36/gal (dryland) to \$0.55/gal (irrigated) with sale of seed meal at \$0.07/lb and fermentation by-products at \$0.035/lb. Another interpretation is that the cost estimates could be increased by 39 percent for dryland production or 17 percent for irrigated production without incurring negative net revenues if the sales price of both oil and ethanol is \$0.75/gal and both seed meal and fermentation by-products are marketable at \$0.07/lb and \$0.035/lb, respectively.

Comparison With Common Crops in New Mexico

Similar analyses were carried out for selected conventional crops commonly grown in MLRA 77 on the aquifer in Curry County, New Mexico: irrigated corn, grain sorghum and wheat, and dryland grain sorghum and wheat, to put the buffalo gourd analysis into context. The results can be summarized as follows. Exclusive of land charges, only dryland and flood-irrigated grain sorghum and flood-irrigated corn have positive net revenues of \$54/acre, \$32/acre, and \$6/acre, respectively. These values are based on optimistic yield data to ensure that comparisons with the buffalo gourd are conservative. These net revenues may be roughly compared to \$137/acre and \$70/acre, respectively, for dryland and irrigated buffalo gourd.

When land charges are included, none of the common crops has a positive return to risk, with only dryland grain sorghum having a value significantly above a negative \$60/acre. If these same land charges are applied to the net revenue values for buffalo gourd, the return to risk becomes approximately \$72/acre and negative \$60/acre for dryland and irrigated production, respectively.

Estimated cultivation costs were then compared with the corresponding buffalo gourd cost estimates. Optimistic yield values were chosen for the traditional crops, and conservative estimates were made for buffalo gourd production. When land charges are excluded, the estimated cultivation cost of buffalo gourd-based liquid fuels is 72 percent, 60 percent, and 50 percent lower than wheat, corn, and grain sorghum-based fuels, respectively, when grown on flood-irrigated acreage. For dryland farming, the estimated buffalo gourd cost is 80 percent and 73 percent lower than for wheat and grain sorghum, respectively.

Conclusion

Buffalo gourd is an attractive candidate for development as an economic crop to produce seed oil and root starch for diesel fuel and fuel ethanol, respectively. Preliminary economic analysis indicates that net revenues and returns to risk are substantially higher for buffalo gourd than for common crops of the High Plains of New Mexico, based on conservative assumptions.

(The complete paper, including tables, figures, and references, is available from the authors.)

CHINESE TALLOW TREE AS A DIESEL FUEL SOURCE

E. B. Shultz, Jr.^{1/} and H. W. Scheld^{2/}

ABSTRACT

The Chinese tallow tree is well adapted to wet regions along the Gulf and South Atlantic coast. It matures rapidly, produces seeds prolifically, and is unaffected by insects and disease. It is possible that, with development of improved varieties, a Chinese tallow tree crop may yield more total fat and oil per acre than the oil palm. The tallow (outer seed coat fat) and the kernel oil might be utilized as diesel fuel extenders in an emergency if the necessary research and development is carried out in advance of the need. Although the tallow has a desirably low iodine value (IV), it is a solid at room temperature. By contrast, the kernel oil is a liquid but has an undesirably high IV, so cannot be used directly. There are several technical approaches discussed herein that might deal adequately with these problems.

BACKGROUND

The Chinese tallow tree, Sapium sebiferum (L.) Roxb., may be the most attractive novel perennial oilseed crop presently under development in the United States because of characteristics such as rapid maturation, prolific seed production, and resistance to insects and disease. Yields from wild trees in Texas (Potts 1946) indicate that more fat and oil might be produced per acre than from the Malaysian oil palm, the current world leader of commercial oilseeds in terms of yield.

With our co-workers we have presented considerable information in recent years on this remarkable tree (Scheld et al. 1980, Scheld and Cowles 1981, Scheld et al. 1982a, Scheld et al. 1982b, Scheld 1983, Shultz et al. 1982a, Shultz et al. 1982b). The present contribution is an effort to call attention to the complexities of using the solid tallow (outer seed coat fat) and the liquid kernel oil of the seed as diesel fuel extenders. These complexities are caused by the peculiar fatty acid compositions of these two very different fatty materials.

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The tallow is largely saturated, composed principally of two conventional triglycerides, palmitic-oleic-palmitic and palmitic-palmitic-palmitic, according to Hirayama and Ohama (1965). Kleiman (1981) has found that palmitic acid predominates at 66 to 76 percent, and oleic acid accounts for 22 to 32 percent. Minor amounts of linoleic and stearic acid are present.

The kernel oil, by contrast, is a complex mixture of conventional triglycerides, largely unsaturated (about 70 percent) with about 30 percent rare unsaturated estolides (tetraester triglycerides). Two unusual short-chain fatty acids ("HODA" and "DDA")^{3/}are present in the estolide fraction of the kernel oil. The fatty acid compositions of the conventional triglyceride fraction and the estolide fraction of the kernel oil are given below:

<u>Conventional</u> <u>triglyceride fraction</u> ^(a)		<u>Estolide fraction</u> ^(b)	
18:3	54.9%	18:3	29.1%
18:2	24.3	18:2	20.2
18:1	13.3	18:1	10.8
16:0	5.7	16:0	5.1
18:0	1.8	18:0	1.5
	100.0%	HODA	16.7
		DDA	16.7
			100.1%

Further, it is helpful to know that although there is considerable diversity apparent, the percentages of tallow and kernel oil are roughly similar. For example, Potts and Bolley (1946) reported 20.3 wt percent oil and 23.9 wt percent tallow in seed collected in the Houston, Tex., region.

The technical problems of using vegetable oils in diesel engines are considerable. Although their heating values are not much lower than those of diesel fuel, vegetable oils are more viscous and less volatile than diesel fuel, as may be expected from their substantial differences in molecular weight and chemical structure. Therefore, use of vegetable oils typically leads to coke deposition on and in the injector nozzles, ring sticking, and by-passing of unburned fuel to the crankcase where polymerization may occur. The high viscosity and low volatility of vegetable oils can lead to poor atomization and inadequate mixing with air, and this is immediately followed by pyrolysis, and/or loss of uncombusted fuel. The presence of double bonds in the vegetable oil leads to oxidative polymerization in the crankcase environment, if the vegetable oil should escape past the piston rings. These problems are not as severe in the indirect-injection (pre-combustion) type of diesel engine, which is more tolerant of a diversity of fuel characteristics, as they are in the direct-injection engine. The presence of the pre-combustion chamber promotes the mixing of fuel and air, allowing fuels of somewhat lower quality to be

^{3/}HODA = 8-hydroxy-5,6-octadienoic acid

DDA = 2,4-decadienoic acid

(a) From Christie (1969)

(b) From Christie (1969) with adjustment of reported DDA content to include presence of HODA.

utilized, in comparison with the direct-injection diesel engine. Unfortunately, the direct-injection engine is typical of agricultural diesel equipment, the most likely market for seed oils as diesel fuel extenders.

Several remedies for these problems have been advanced and are being investigated by many organizations (ASAE 1982). Viscosity can be reduced by mixing with ethyl alcohol, with or without an emulsifier. If emulsifier is not present, continuous mixing of the vegetable oil and alcohol mixture may be necessary to prevent the separation of these immiscible fuels. Viscosity can also be reduced somewhat by heating of the vegetable oil fuel or by mixing of the vegetable oil with a large proportion of diesel oil with which it is miscible. Vegetable oils can also be transesterified to methyl or ethyl esters of the component fatty acids, with glycerol as a by-product, and the simple esters used as diesel fuel. Because such esters are of much lower molecular weight than triglyceride oils, viscosities can be lowered, in effect, by this chemical conversion method. In addition, it is possible to reduce the numbers of double bonds by partial hydrogenation, to cut down on crankcase polymerization problems. It should be noted, however, that each of the foregoing approaches to solving the diesel utilization problems of vegetable oils carries with it a set of its own problems, and the outcome of studies in these fields is still uncertain. With this background in mind, let us consider the diesel fuel potential of Chinese tallow tree tallow and kernel oil.

TALLOW AS DIESEL FUEL

The tallow is a solid of low IV at room temperature. The melting point is about 38°C (100°F). Because the tallow contains few double bonds, problems of polymerization of unburned tallow in the crankcase can be expected to be minimal. The main difficulty will be in keeping the tallow molten, well above 100°F in fuel tank, fuel lines, pump, injector, etc. The practicality of doing this may be questionable, and it may be preferable to consider mixing the tallow with other, more unsaturated vegetable oils (perhaps kernel oil), or with an alcohol and emulsifier, or with diesel fuel. Experiments would need to be carried out to establish the feasibility of mixed triglyceride fuels encompassing a wide range of levels of unsaturation, represented by large differences in iodine value. In short, a combination of heat, and mixture with other vegetable oils, alcohol, or diesel fuel, might provide a fuel mixture of acceptable viscosity and volatility. Of course, the transesterification option is also possible.

KERNEL OIL AS DIESEL FUEL

In the case of the kernel oil, a different set of problems arises, mainly related to the highly unsaturated nature of the oil. The IV is about 170 (Hirayama and Ohama 1965) well above the 145 limit suggested by Pryde (1981, 1982), and even higher than the IV of linseed oil (about 155), which is a known varnish-forming oil. This might be dealt with by partial hydrogenation, to drop the IV value below 145, or by mixing the kernel oil with low IV fats, or by mixing with high percentages of diesel fuel. Without one or more of these procedures, it would seem unlikely that kernel oil would prove

acceptable in diesel engines. Again, the transesterification option is available, as is mixing with alcohol, to reduce viscosity.

KERNEL OIL AS DIESEL FUEL AFTER REMOVAL OF HODA AND DDA

Another concept that requires experimental investigation is the conversion of the entire kernel oil to fatty acid esters and removal of the esters of the rare short-chain fatty acids, HODA and DDA. These might be reserved for higher valued applications, and the esters of all the other fatty acids might be utilized as diesel fuel-blending materials. These would be largely the esters of 18-carbon unsaturated fatty acids (linolenate, linoleate, and oleate) with some palmitate and stearate in approximately the following percentages, estimated by calculation, assuming 100% removal of HODA and DDA from the kernel oil:

linolenate	52
linoleate	25
oleate	14
palmitate	7
stearate	2

MIXED TALLOW AND KERNEL OIL AS DIESEL FUEL

If the tallow and kernel oil were to be used as a mixture for diesel fuel extender, the whole seed might be crushed to produce a mixed oil. A single extraction with hexane might be carried out. Alternatively, the whole seed might be screw-pressed, but yields would be lower than in hexane extraction. Although the average IV of the mixed fat and oil would be in the acceptable range, the presence of the high-IV kernel oil may still cause polymerization problems. The aforementioned remedies (mixing with alcohol or diesel fuel, esterification, partial hydrogenation) should be investigated.

CONCLUSIONS

From a technical viewpoint, in the absence of economic analysis, it is possible at this time to regard tallow and kernel oil, separately and mixed, as potential diesel fuel extenders, under the diversity of conditions described above. In all cases, further research including long-term durability tests would be required before suitable operating conditions and fuel mixture compositions may be specified with confidence. However, because tallow and kernel oil may bring higher prices in other markets, their use as diesel fuel extenders might be considered only for emergency purposes. It must be stressed that fuel research and economic analyses will be needed and that such studies must be completed and information disseminated before an emergency appears.

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PROGRESS IN DOMESTICATION OF THE CHINESE TALLOW TREE SAPIUM SEBIFERUM

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ABSTRACT

Research is under way in several areas crucial to the development of the Chinese tallow tree as a perennial oilseed crop for poorly drained areas of the Southern United States. A large number of seed source trees has been selected for study of the genetic basis for productivity, flowering and growth patterns. Tallow and oil analyses of trees from the Houston, Texas area indicate quantitative and qualitative differences in fat components of individuals and suggest the feasibility of selecting and propagating strains tailored for specific high-value markets. Methodology is under development for mass multiplication of elite specimens by aseptic micropropagation and for large scale plantation establishment with clonal materials.

INTRODUCTION

The Chinese tallow tree Sapium sebiferum has been naturalized in parts of the Southern Coastal U.S. for nearly 200 years. It is capable of competing with native species in soils that are saline, poorly drained or subject to intermittent flooding, and continues to extend its range, invading and establishing vigorous natural forests in such land areas. Culture of the tallow tree as a crop plant is said to have begun in China over a thousand years ago. Most of the naturalized stock in the U.S. originated from unsuccessful attempts to establish the tree as a crop, probably with the best growing stock available

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at the time. So-called wild trees now found in the U.S. are only briefly removed from stock selected over a long period of time and constitute a significant head-start toward the domestication of the tree in the U.S. However, all of the past efforts at introduction of the Chinese tallow as a crop have been carried out empirically with minor attention to the important technical aspects. The primary concern of the current effort has been with the acquisition of the data and technology base necessary for development of the tree as a modern crop plant.

RATIONALE OF THE DEVELOPMENT EFFORT

There is potential for economic return from the tree managed as a wood crop (Scheld and Cowles, 1981), as honeybee forage and as an oilseed crop (Scheld, et al., 1983); the strategy chosen for development of the crop assumes that the primary economic niche of the Chinese tallow is that of an oil-seed crop targeted for land that is considered marginal or unsuitable for conventional crops.

A labor-intensive culture system for Chinese tallow has been operational in China for many centuries. As a consequence, cultural characteristics such as growth form and ripening have been selected to fit a labor-intensive system. Moreover, it appears that in recent years the culture system has evolved toward the selection of cultivars and the use of cultural practices that reduce hand labor costs by encouraging the growth of relatively small numbers of very large seed clusters (Zhang, 1983). The net effect has been a sacrifice of some of the yield potential of the tree. In the U.S. there is no current basis for culture of the Chinese tallow in terms of either suitable growing stock or an appropriate agronomic system. The crop development effort, reduced to simplest terms, has been concerned with optimization of the seed components and crop configuration keeping two major considerations in view as the effort has evolved:

Because of the unique form and unusual nature of the fatty components of the Chinese tallow seed it is expected to fit the economic niche of a specialty seed oil aimed at specific high-value market areas and tailored by a selection and breeding program to the requirements of these markets.

The agronomic system for the crop must conform to the pattern set by U.S. field crops in general with dependence for profitability upon high yield, large scale and mechanization of cultivation and harvest with a consequent requirement for uniformity of form, growth rate and ripening.

RESEARCH EFFORTS

Operationally the development effort has been carried out as several distinct but mutually dependent biological and chemical studies that were considered crucial in determining the viability of the Chinese tallow tree as a crop plant. Research has been at a relatively basic level in order to provide the broadest possible base for the development effort.

Ecological Studies

A continuing effort to understand the ecological relationships of the plant and to assess the potential for development of insect or disease problems is a necessary part of any crop system. In the case of the Chinese tallow, the question of environmental impact becomes more critical because large areas formerly occupied by grass or low shrub would be converted at considerable expense to permanent stands of trees. The Chinese tallow is notably insect- and disease-free; presumably because it contains in its tissues significant amounts of materials toxic or repellent to insects. Thus, in addition to understanding the mechanism(s) of this resistance and whether it is likely to remain in effect over an extended period of time, there is also a question of whether the release of possibly toxic materials from large areas of tallow tree crop land could have an environmental impact.

Studies of the ecology of Chinese tallow forest have been carried out over a period of several years. Results obtained indicate some toxic effect of leaf leachate upon the animal component of the ecosystem but no apparent effect upon plant associations bordering the tallow forest. Over a long period of observation no obvious insect pests have been found, and there is no monoculture effect with respect to insect populations; merely fewer kinds of insects in tallow tree forest as well as smaller numbers. Future research will be aimed at understanding the mechanisms of insect resistance and detecting potential for future development of insect pest associations.

Seed Chemistry

The study of the seed chemistry has been approached in several ways. Preliminary studies assessed the methodology for processing with emphasis upon separate recovery of tallow and oil components of the seed (Engler, 1980). Subsequently, the major thrust of the work has emphasized the genetic variability in seed fat chemistry (Scheld, et al., 1983), and the potential for selection of commercially valuable stock (Shultz et al., 1982).

The peculiar chemistry of the seed fat components has been examined in the light of potential markets or uses and the inherent chemical and morphological variability of the extant population of seed-bearing trees. Feasibility studies on potential products from the seeds of the Chinese tallow tree have been underway at Washington University in St. Louis for several years. Figure 1 summarizes the findings of these studies and indicates major potential products other than fuels. It is noteworthy that the tallow of the Chinese tallow tree is dominated by one triglyceryl fraction, the triglyceride of palmitic and oleic acids (POP) having oleic acid esterified to the center hydroxyl, and that 98 percent of the fatty acids are palmitic and oleic. In addition to food uses, the tallow can be thought of as a source of high-purity oleic and palmitic acids for a number of industrial purposes. Of major importance in the case of the kernel oil is the significant percentage of two rare, short-chain fatty acids, HODA¹ and DDA,¹ from which several novel products

¹HODA = 8-hydroxy-5, 6-octadienoic acid
DDA = 2, 4-decadienoic acid

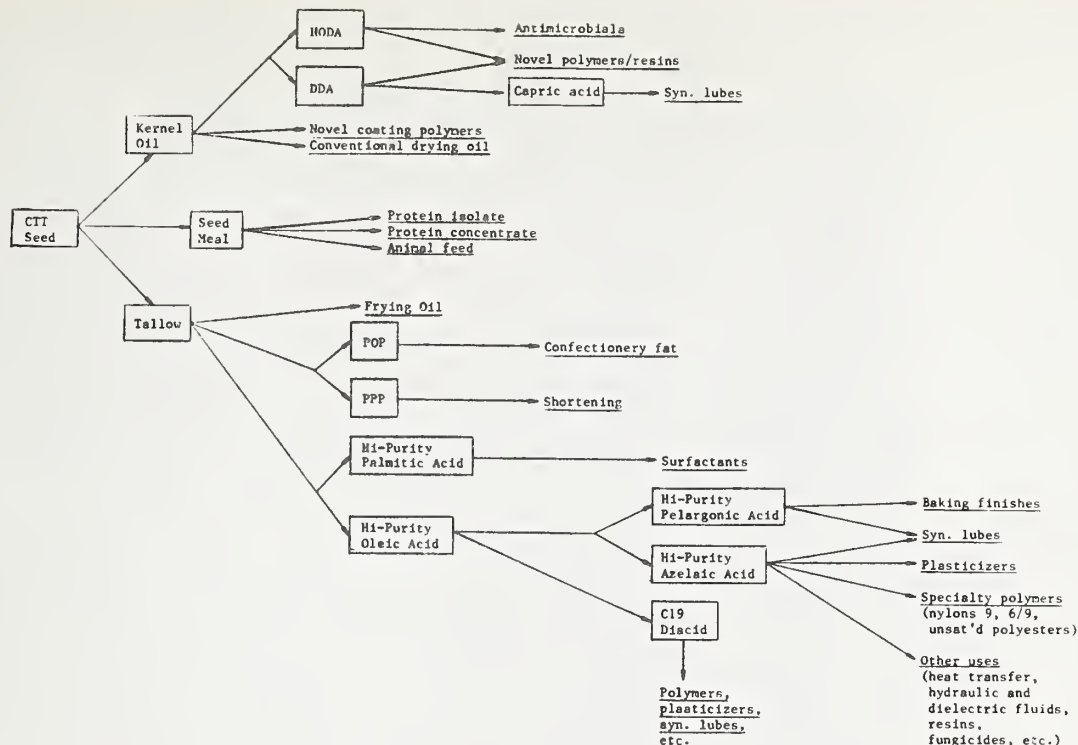


Figure 1. Product cascade: Major potential industrial products from the Chinese tallow tree.

might be derived. Individual trees having exceptionally high proportions of POP or short-chain acids (Shultz, et al., 1983; Shultz, et al., 1982) have been selected for propagation research.

Genetic Characterization

In the populations of naturalized Chinese tallow growing in the U.S., the most striking feature is the extreme variability among individuals with respect to every observable characteristic. The existence of such variability is the basis for our expectation of success in developing a crop plant or plants having the desired properties. There are, however, no published descriptions of genetic variability in the Chinese tallow, and it has only recently become known that the Chinese tallow has a complex and unusual breeding system that effectively forces outcrossing. A study of the genetics of Chinese tallow has thus been carried out in support of the general crop improvement effort.

Two major methodological approaches have been taken. In the first, samples of flowers, leaves and seeds were taken from the tallow tree population in several areas of the country: Texas, the East Coast (North Carolina to northern Florida) and California. These were studied for genetic variation via electrophoretic analysis of variation in enzymes coded by selected gene loci. In the second approach, a multivariate analysis of morphological and phenetic variation was undertaken for a population of trees in a single locality. Variables studied were primarily those related to productivity: leaf

size, shape and chlorophyll content; tree configuration and flower characteristics related to seed production. In a separate but related study, seeds from this same population were analyzed for variation in fatty acids of the oil and tallow components. The results of these studies have been reported previously (Scheld, et al., 1983; Shultz, et al., 1982).

The genetics of Chinese tallow is complex. There is some morphological difference among populations from different localities, but variability among individuals within a given locality is greater. This pattern is reflected in electrophoresis data in which patterns of electrophoretic variation of samples from different localities are similar, but localities differ in presence and proportion of low-frequency allozymes. Future work will continue to examine the basic genetics as well as the special relationships of the desirable crop plant characteristics.

Propagation

Because the Chinese tallow shows a great deal of variation among individuals, there is high probability for discovery of useful variants. However, because of the outcrossing mechanism inherent in its flowering pattern, propagation from seed will not reliably transmit the selected properties. A vegetative method of propagation is therefore needed in order to conserve parental genotypes in subsequent generation and will play a decisive role in multiplication of elite specimens as well as in germplasm maintenance and storage.

Propagation of Chinese tallow from cuttings is seldom successful, for even though some roots may form after an extended period of time, they are not vigorous and fail to sustain growth. The only reliable vegetative method thus far devised for Chinese tallow is grafting which, if dependent upon traditional propagation techniques for scion stock, will result in inordinately slow expansion of orchards. The only realistic approach to the desired objectives is by the use of aseptic culture procedures--so called "tissue culture."

There are a number of good reasons for believing that tissue culture techniques would serve well in the development of Sapium as a modern crop plant. The way the tree grows suggests high susceptibility to micropropagation; it coppices very well, and injured trunks and branches produce "suckers". The stimulation of precocious branches via aseptic culture frequently encourages increased bushiness of habit in the resulting plant material. Cultivation of the plant as a modern crop will very likely be in hedgerow form. If bushiness is sustainable in the mature tree, susceptibility to hedging will improve. Further, in some tree species the time to flowering may be shortened and the usual juvenile stage abbreviated in precociously branched material. Thus aseptic culture techniques can perform a useful function in engineering desirable cultural characteristics as well as permitting rapid multiplication.

At Stony Brook considerable success has been achieved in the aseptic culture of some, but not all, strains of Chinese tallow. It is not uncommon to encounter differences in responsiveness to aseptic culture procedures according to the genetic background of the material. In this regard, the Chinese tallow is no exception. Figure 2 summarizes the procedures followed in micropropagation or multiplication from mature trees. While we have shown

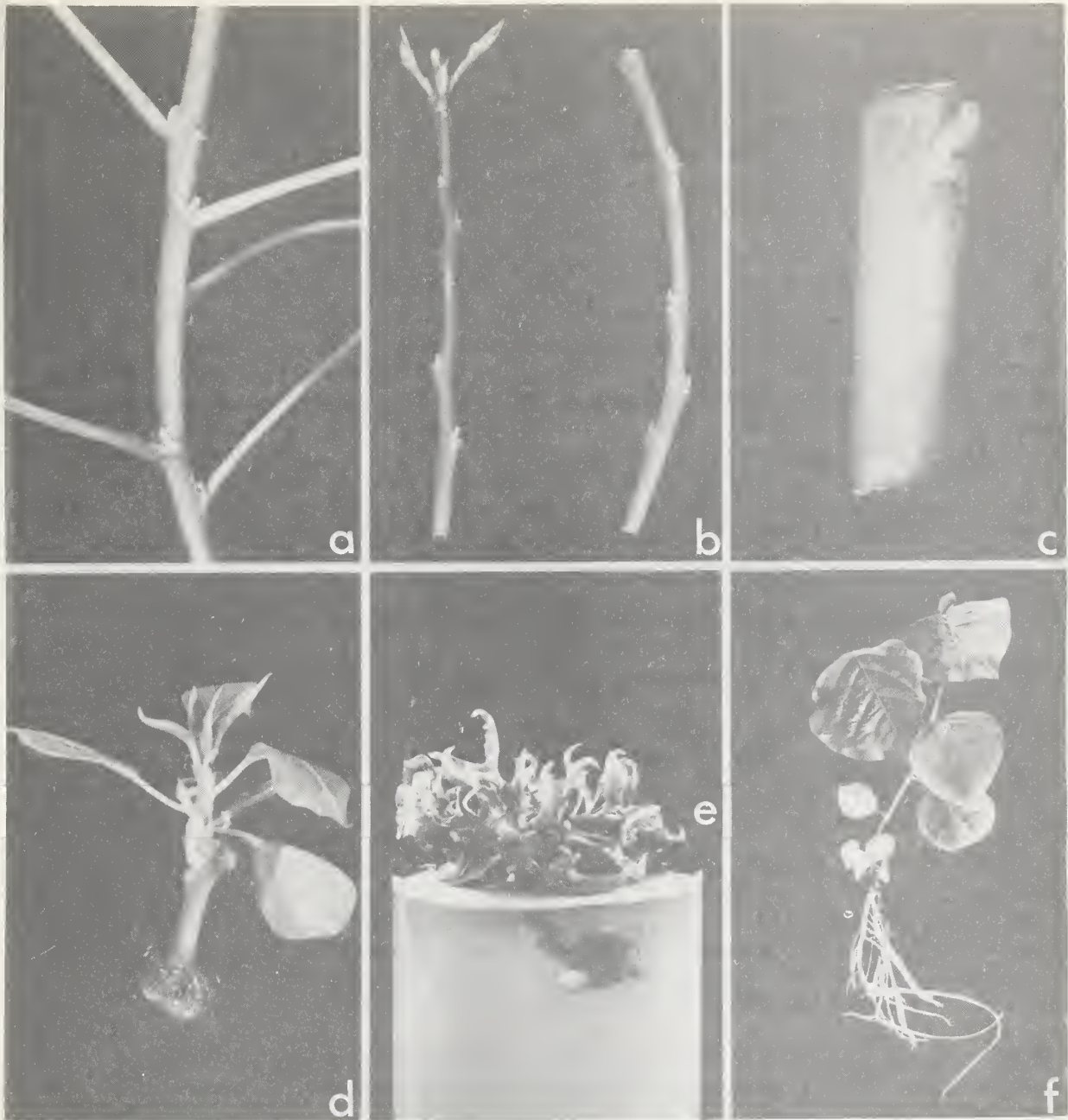


Figure 2. Sequence of procedures in photographs followed in the multiplication of Sapium from explanted lateral buds. (a) Young branch showing size and stage of development of buds used for primary explantation; (b) same, prepared for sterilization after removal of petioles and cutting to size; (c) typical primary explant ready to be placed on nutrient medium; (d) typical explant after 25 days growth; (e) another after 57 days growth and a single subculture; (f) rooted plantlet (unpublished work of Krikorian and Kann).

that such methods have real potential, much research still needs to be done to extend the existing protocols to a wider range of germplasm or to develop new regimens. Moreover, problems related to subsequent stages such as "hardening off", the transplanting of aseptically produced plantlets to the field and their evaluation under field conditions need to be addressed.

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FUELS FROM THERMAL DECOMPOSITION OF VEGETABLE OILS

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ABSTRACT

Thermal and catalytic decomposition of vegetable oils to produce substitutes for gasoline and diesel fuel has been studied by a number of researchers using a variety of methods. These studies are summarized in this paper. The majority of studies had the objective of finding a gasoline replacement, but the fuels obtained possessed an inferior octane number. At the present, a hydrocarbon fuel with a similar volatility and molecular weight as diesel fuel has been produced with an approximate volume yield of 50 percent from the decomposition of a vegetable oil.

INTRODUCTION

Certain problems with viscosity and volatility are present in the direct use of vegetable oils as diesel fuel that prevent direct substitution for diesel fuel without modifications to the engine. Past studies have suggested that by thermal or catalytic decomposition of the vegetable oil, a partial hydrocarbon fuel of the volatility of diesel fuel can be obtained. Until recently, most of the investigations into the thermal degradation of vegetable oils were from the 1920's to the 1940's, primarily in countries where the production of vegetable oils was large or the reserves of mineral fuels were small. The initial investigation was by Engler [7] who in 1888 attempted to synthesize petroleum from vegetable oils in order to establish the theory of the origin of petroleum from organic matter. In all of the early work and nearly all of the more recent research, the primary goal was to obtain the greatest amount of gasoline substitute with little regard for obtaining a diesel fuel substitute. Therefore, little direct investigation of obtaining diesel fuel from vegetable oils by thermal degradation has been done, but the previous research may still be helpful in providing guidance for the production of diesel

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fuel. The purpose of this paper is to provide a brief overview of what has been attempted and the results obtained in the thermal and catalytic decomposition of vegetable oils.

EXPERIMENTS PERFORMED AND RESULTS

Essentially three different methods of processing vegetable oils to obtain fuels have been used: (1) passing of the oil over a heated catalyst in a tube, (2) distillation of the oil while in the presence of metallic salts, and (3) distillation of the oil under pressure or distillation of the oil followed by vapor-phase cracking. In some studies, the vegetable oil was first converted to soaps by hydrolysis and then processed by the above three methods. Most of the research has been conducted using the first two methods.

The pioneering work using catalysts and/or metallic salts was performed by Mailhe in the early 1920's. Mailhe passed linseed oil vapors over heated balls of Cu mixed with MgO, Al_2O_3 or kaoline at 550 to 600°C [11], colza oil over Cu- Al_2O_3 in a Cu tube at 550° to 650°C [12], oleic acid [13] and shark oil [14] over a Cu-Al catalyst in a Cu tube at 600 to 650°C, and obtained gas and liquid products of a brown color and strong odor. He investigated the action of metallic chlorides by heating vegetable and animal fats, tallows, etc., with a ratio of 5 to 10 percent $ZnCl_2$, $CaCl_2$, $MgCl_2$, $BaCl_2$, $SnCl_2$, NaCl, and quick lime to 450°C and obtained paraffins and olefins similar to petroleum [15,16]. Work with castor oil [17,18] decomposed at 540° to 570°C in a Cu tube containing Al demonstrated that castor oil behaved differently from the other oils in that enanthylic aldehyde was formed. Heating 300 g of peanut oil [19] and 50 g of anhydrous $MgCl_2$ in a Cu kettle produced 66 percent of neutral distillation products with hydrocarbons ranging from methane to heavy lubricating oils present. In all cases, he observed free fatty acids in addition to hydrocarbons present in the liquid produced.

Gallo and Correlli [8] used a method similar to Mailhe in 1923 by passing vegetable oil, decomposed by superheated steam in the presence of alkali earths, over FeO catalyst at 550 to 600°C. They found similar products to those of Mailhe.

A process patented in Britain in 1932 [30] used activated carbon in the form of fibers heated to 350°C and yielded a conversion of 75 percent of the vegetable oil to a liquid that contained hydrocarbons with a boiling range from 110° - 250°C. Unspecified gases were also produced.

Sato and Tseng, in Japan, [25,26] mixed soybean oil with Mg or Ca oxides and carbonates before distilling the mixture and demonstrated that Mg produced a superior fuel and that the carbonates took longer to distill than the oxides. They also found that the Mg and Ca soaps of soybean oil produced heptane, octane, and nonane, but the existence of aromatic hydrocarbons was not confirmed. Tokunaga [27], also of Japan, used a catalyst composed of one or more of activated acid clay, silica gel, Al_2O_3 , or bentonite, and one or more of Th, V, Ce, Ni, Co, Fe oxide or hydroxide and obtained olefins, saturated hydrocarbons, aldehydes, and ketones after distillation.

The effect of the addition of lime on the cracking of tung oil was studied by Chang, Shiah, and Chan [4]. The amount of lime had little effect on the gasoline yield, and the maximum yield of liquid products was obtained when 3.7 percent lime was used.

Another process patented in 1948 [22] utilizing the soap of a vegetable oil claimed that a 97 percent hydrocarbon oil was obtained, 28 percent in the gasoline boiling range, and 72 percent of a heavier oil. The use of the soap enabled processing at lower temperatures.

Ping [23] in China took nine vegetable oils of varying degrees of unsaturation, decomposed the oil with 1 percent (by weight) of aluminum chloride and obtained a liquid distilling above 250°C with the following properties: specific gravity at 20°C of 0.865, viscosity (Redwood) of 40 sec at 100°F, and flash point of 125°C. The yield of light oil was found to be independent of the unsaturation of the oil. Koo and Cheng [10] decomposed china wood (tung oil), soybean, cottonseed, and rapeseed oil using NaOH at 800°F, obtaining 52.7 percent gasoline fraction. Without a catalyst at 1000°F, they obtained 40 percent gasoline fraction.

In India, Dalal and Mehta [5] "cracked" vegetable oil in tubes of Fe and glass at various flow rates and also distilled vegetable oil in the presence of various proportions of ZnCl_2 . They found that the percent of the oil that "cracked" increased with temperature, decreased with an increased amount of ZnCl_2 , ZnCl_2 was more effective than CaCl_2 , and that the amount of decomposition is a function of the unsaturation of the oil. As the iodine value or degree of unsaturation of the oil increased, the amount of distillate decreased and the volume of gas and residue increased. The vegetable oil that was decomposed in the tubes of Fe and glass, the percent of the vegetable oil "cracked," increased with a decreased flow rate through the tubes. Mandlkaar and co-workers [20] found that the percent of crude diesel fuel decreased with an increase of zinc chloride from 0.5 to 2.5 percent when sesame oil was distilled. Goswami and co-workers [9] discovered that pyrolysis of oleic acid at 350 to 385°C over a Cu catalyst resulted in a 50 percent conversion to mixed hydrocarbons, 49 percent of them distilling from 250 to 350°C.

From the early 1950's until 1978, few studies on the catalytic decomposition of vegetable oils to produce fuels are recorded. In 1978, a U. S. patent [24] was issued for a process for producing hydrocarbons by "thermolyzing" the oil in the presence of a silica-alumina catalyst impregnated with an oxide of the transition metals of groups IIA, IIIB, IVB, VB, VIB, VIIB, and VIII at temperatures between 300° and 700°C at atmospheric pressure. The process described produced a product free from oxygenated compounds other than CO_2 and H_2O .

The shape selective ZSM-5 type zeolite catalyst has been used to produce a high-grade gasoline from crude vegetable oils [28]. After an initial thermal conversion to smaller molecules, the zeolite catalyst was used to restructure the molecules to the desired gasoline product. With corn oil at 450°C and atmospheric pressure the product obtained was separated into four categories, and the approximate amount produced was fuel gas and LPG, 20 percent; gasoline, 60 percent; and light distillate, 12 percent.

Another recent study in Brazil by Anjos, Gonzalez, Lam, and Frety [2] looked specifically at the production of diesel fuel from the catalytic decomposition of soybean oil. The soybean oil was heated to 300°C and passed over Al_2O_3 -S at 300°, 400°, and 500°C. The liquid products were analyzed by infrared spectroscopy and by chromatography and compared to a typical diesel fuel. The effect of the degree of unsaturation of the oil was evaluated by hydrogenating the oil to iodine values of 10 and 60 compared to the crude soybean oil's iodine value of 120. The hydrogenated oils gave a lower liquid yield and the weight of the residue fell slightly, but the amount of hydrocarbon obtained increased from 28 percent for crude soybean oil to 40 percent. The oil with an iodine value of 10 contained no detectable liquid products with oxygen groups compared to 25 percent for the unhydrogenated crude soybean oil's liquid products. The most saturated oil yielded an oil of approximately the same mean molecular weight as diesel fuel; whereas the less saturated oils yielded a much lower mean molecular weight oil.

Thermal degradation by distillation under pressure was the method used in 1932 by Morrell, Egloff, and Faragher [21]. They "cracked" Niger and Sumatra palm oils under pressures from 50 psi to 135 psi and observed that the amount of crude diesel fuel produced increased with a decrease in pressure with a maximum yield of 25.4 percent for Sumatra and 40.9 percent for Niger palm oil at pressures of 75 psi and 50 psi, respectively. Egloff and Morrell [6] "cracked" cottonseed oil and obtained over 54 percent of a refined gasoline-like fuel with an octane number of 55 when distilled under 135 psi pressure. The hydrocarbon analysis by the Egloff-Morrell method of the gasoline-like fuel yielded paraffins, 37.1 percent; unsaturates, 27.1 percent; naphthalenes, 9.9 percent, and aromatics, 25.9 percent.

Dalal and Mehta [5] and Mandlekar, Mehta, Parekh, and Thosar [20] also pressure distilled a variety of oils in India using the Egloff-Morrell distillation method. Under 45 psi pressure, the two studies obtained a crude diesel fuel (that distilling above 225°C) of the following amounts from the oils: groundnut, 61 percent; mowrah, 66.2 percent; coconut, 74.74 percent; sesame, 63.65 percent; cottonseed, 57.12 percent; and castor, 48.5 percent. Again, the amount of crude diesel fuel obtained decreased as the pressure was increased.

In China, Chang and Wan [3] pressure distilled tung oil and distilled the calcium soaps of rapeseed, peanut, and tung oils to produce a "motor fuel." An experimental conversion and refining plant was proposed capable of producing 73 percent by weight diesel oil of Saybolt viscosity of 40 sec. at 100°F, flash point of 150°F, and no detectable sulfur. The vegetable-diesel fuel was tested in an unspecified engine, and the brake horsepower obtained was 90 to 95 percent and the fuel consumption 113 to 115 percent of that obtained with pure diesel fuel.

A British patent [29] described obtaining "motor spirits" by vaporizing vegetable oil and passing the vapor through a cracking plant operated at a temperature of 500 to 650°C and then refining the products by fractional distillation.

Recently, Alencar and co-workers [1] in Brazil took palm, piqui, and babassu oils and performed the pyrolysis of the oils in the absence of a catalyst for four hours at 300°C. The resulting distilled liquid was analyzed by GLS-MS-Computer and found to contain primarily n-alkanes and n-alkenes with an average volume yield of 50 percent.

CONCLUSIONS

Despite economic considerations, the production of a diesel fuel from the thermal processing of vegetable oils appears to hold promise. Only one of the studies mentioned actually used the fuel produced in a diesel engine so the exact behavior of the fuel in a diesel engine is unclear. In addition, much of the research that has been made lacks the sophistication of experimental control and analysis that is now possible, and it may be true that the production of a fuel for diesel engines is even economically possible by the optimization of a previous method. At the present, the method that appears most promising is pre-hydrogenation, followed by thermal or catalytic decomposition of the vegetable oil.

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ECONOMICS

ECONOMICS OF USING DIVERTED ACRES TO PRODUCE SUNFLOWER OIL FOR FUEL

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INTRODUCTION

Vegetable oil prices are currently higher than diesel fuel prices and are likely to remain so for the foreseeable future (U.S. Dept. of Energy 1983). Subsidies will be needed to make vegetable oils competitive with diesel fuel. However, it may be possible to subsidize vegetable oil without incurring additional government outlay. Farm commodity programs offer inducements to producers to idle land from the production of surplus commodities. Many producers will accept smaller inducements to cut production of surplus commodities if they are allowed to shift acreage to oilseed crops for fuel. The savings in government payments may be enough to subsidize vegetable oil to make it competitive with diesel fuel.

No adverse affect on oilseed prices should occur if a quantity of oil equal to oilseed production on diverted acres is removed from the commercial market for use as a fuel. However, oilseed prices may be affected if the oil meal produced depresses meal prices.

The dominant oilseeds produced in the United States are soybean, cottonseed, peanut, and sunflower. Unlike sunflower, most of the value of soybeans and cottonseed are derived from nonoil products. Therefore production of sunflower for fuel would less seriously depress the prices of the nonoil products. Sunflowers have an advantage over peanuts because they can be produced with less specialized equipment and are adaptable in a wider geographic area. Peanut oil is also the most expensive of the major vegetable oils.

The potential advantages of using land idled under government programs to produce sunflower oil for diesel fuel are (1) no additional government expenditures, (2) reduced use of petroleum, an exhaustible resource, (3) improvement in U.S. balance of payments through reduced petroleum imports, (4) increased use of sunflower oil-crushing capacity, which is currently at a low level of utilization, and (5) increased business activity in affected rural communities.

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SUNFLOWER OIL SUBSIDIES

The minimum amount of refining of sunflower oil for use in diesel engines is degumming along with filtration to remove particulate matter (Bruwer, et al. 1981). The most practical means of reducing the undesirable fuel characteristics of sunflower oil is to mix it with diesel fuel. A mixture of sunflower oil and diesel fuel also avoids the added expense of refining out waxes that would be absorbed in the diesel portion of the mixture. A sunflower oil:diesel fuel mixture containing from 10 to 30 percent crude degummed sunflower oil is considered a practical range for consumer acceptance.

The cost of refining gums out of crude sunflower oil according to industry sources is about 2-1/4 cents per pound or 17.3 cents per gallon. Adding this to the April 1983 wholesale price of raw sunflower oil of \$1.72 per gallon brings the price of degummed sunflower oil to \$1.89 per gallon.

The sunflower oil:diesel fuel mixture would have to be priced below diesel fuel because of the lower energy value of the sunflower oil portion, 92.9 percent, and the other potential problems. For example, manufacturers will not guarantee engines if a fuel mix containing vegetable oil is used. A 20:80 sunflower oil:diesel fuel mixture would have to sell for 98.5 percent of the price of diesel fuel to be equivalent on an energy basis. At the current retail price of diesel fuel of \$1.05 per gallon, the energy equivalent price of 20 percent sunflower diesel fuel mixture would be \$1.034 per gallon. Subsidies on sunflower oil needed to reduce the price of various fuel mixtures to selected levels are given in table I.

Table I.--Subsidies on sunflower oil that reduce the price of selected sunflower oil:diesel mixes to given levels

Fuel Mix Sunoil:Diesel	Price Per Gallon of Sunflower Oil ¹ :Diesel ² Mix			
	\$1.05	\$1.03	\$1.01	\$.99
	-----subsidy needed per gallon-----			
100:0	0.84	0.86	0.88	0.91
25:75	.84	.92	1.00	1.08
20:80	.84	.94	1.04	1.14
10:90	.84	1.04	1.24	1.44

¹Wholesale raw degummed sunflower oil \$1.89 per gallon. Raw sunflower oil 22.35 cents per pound plus 2.25 cents per pound for degumming (7.68 lbs. per gallon).

²Retail diesel price \$1.05 per gallon.

If price discounts are needed, a larger portion of sunflower oil in the mixture would reduce the subsidies required. A lower percentage of sunflower oil in the mix, on the other hand, may increase consumer acceptance due to

quality but would increase government subsidies for price discounts on the mixture. For example to reduce the mixed fuel price by 1 cent on a 25:75 sunflower oil:diesel fuel mixture would require a 4-cent increase in the sunflower oil subsidy, while a 1-cent reduction in a 10:90 mixture would require a 10-cent increase in sunflower oil subsidy.

FARMER PARTICIPATION

The same fixed costs are incurred by farmers whether land is idled or in production. Therefore, anticipated return above variable costs is the relevant figure farmers use to compare cropping alternatives in the short-run perspective of acreage diversion programs. Farmers would participate in a sunflower-for-fuel option on diverted acres if the option improved their return above variable costs. Figures from east central North Dakota, the heart of the sunflower production area, are used to compare benefits and costs of leaving land idle and raising sunflower. Average revenue and variable costs for sunflower and idle land (summer fallow) are shown in table II.

Table II.--Returns and variable costs of summer fallow and sunflower production in east central North Dakota, 1983 estimates

	Sunflower	Conservation Acre Fallow
Returns	\$108.93 ¹	\$24.80 ²
Variable Costs	51.66	9.49
Returns Above Variable Costs	\$ 57.27	\$15.31

¹Yield of 1,170 lbs. at \$.0931 per lb.

²Value of increase in yield potential and the reduction in costs of production the year after fallow.

Fallow has a positive return because the value of reduced inputs and higher yields after summer fallow is more than the cost of summer fallow tillage. Producers will be indifferent between accepting full payment for acreage set-aside or accepting a \$41.97 per acre reduction in government payments to grow sunflower for fuel ($\$57.27 - \$15.31 = \$41.97$). The government savings of \$41.97 could subsidize the 58.6 gallons² of sunoil produced by 71.6 cents per gallon ($\$41.97/58.6$). The 71.6 cents a gallon available to subsidize sunflower oil for fuel is not enough to reduce the price to that of diesel fuel ($\$1.89 - \$.72 = \$1.17$).

However, not all yields within an area are average. Important yield determinants not affecting variable costs such as timeliness of operation and

²(1,170 lbs./acre X .385 oil extraction ÷ 7.68 lbs./gallon).

land quality tend to give high yield producers higher returns above variable costs. The estimated return for a 1,600 pound per acre producer in east central North Dakota is illustrated as follows:

1. Gross Returns 1,600 lbs. @ .093	= \$148.80
2. Variable Costs	59.83
3. Return Above Variable Costs	88.97
4. Return Above Variable Cost of Fallow	15.31
5. Reduction in Government Payment (3)-(4)	73.66
6. Sunflower Oil Yield Gallons/Acre	80.2
7. Sunflower Oil Subsidy Dollars/Gallon	.918

No difference in the value of summer fallow within the area is assumed. The producer who expects a 1,600-pound sunflower yield would gain by accepting up to a \$73.66 reduction in set-aside inducements to grow sunflower for fuel. This reduction could provide a 92-cent per gallon subsidy, for the 80.2 gallons of sunflower oil produced, which is enough to make a sunflower oil: diesel fuel mix less expensive than straight diesel and about equivalent on a BTU of energy basis.

Present price and cost relationships in east central North Dakota make utilization of an option to grow sunflower for fuel on diverted acres feasible only by a few of the most profitable sunflower producers. Procurement of sunflower from other producers would necessitate additional government outlay.

A program to subsidize sunflower oil for fuel from savings in reduced acreage diversion payments would probably be more successful in high yield areas, such as the Corn Belt. The reasons are high sunflower yields and low returns for idled acres.

Returns above variable costs for sunflower are higher in the Corn Belt than in traditional sunflower areas. Harvested sunflower acreage of the 11 south central Minnesota counties averaged only 8,500 acres annually between 1978 and 1981 but yielded 1,622 pounds per acre (Minnesota Agricultural Statistics). Two thousand pound yields are not uncommon.

Benefits of fallow are less in the Corn Belt than traditional sunflower areas. An inverse relationship between net returns of fallow or idled acres and the average productivity of an area exists for two reasons. Higher soil moisture accumulation due to fallow increases yield potential more in drier, lower yielding areas than higher yielding areas where moisture is generally sufficient. Costs of fallow increase for areas of higher precipitation because more expense in tillage operations and/or cover crops are necessary for weed and/or erosion control.

An increase in sunflower prices would not appreciably change the results. Higher sunflower and hence sunflower oil prices would increase the subsidy needed to make sunflower oil competitive with diesel fuel. Higher sunflower prices would make possible a larger reduction in government payments to grow sunflower on diverted acres. A real increase in diesel fuel prices on the other hand would make the proposal more feasible.

OTHER CONSIDERATIONS

Acreage diversion programs vary greatly from year to year. Some years none are needed. For this reason it would not be desirable to construct additional crushing plants to handle sunflower for fuel. Excess capacity would have to exist in the oilseed-crushing industry to handle the sunflower grown for fuel. Capital requirements for equipment to degum sunflower oil are relatively low so this requirement should not hinder implementation of a sunflower-for-fuel program.

The sunflower acreage that could be utilized for fuel is limited to the excess capacity available in oilseed-crushing plants. The existing crushing plants in North Dakota and Minnesota are capable of annually crushing 1,638,000 tons. Total domestic sunflower crush for 1981 and 1982 averaged 482,000 tons or 29.4 percent of commercial crushing capacity. Domestic sunflower plants have generally operated at less than capacity because export demand has mainly been for whole sunflower seeds, not sunflower oil. An additional 1,912,000 acres of sunflower yielding 1,200 lbs./acre would be needed to operate plants at full capacity. Crushing plants for other oilseed crops could, with some modification, process sunflowers, also.

Two million acres of sunflower would produce only 3.7 percent of farm diesel requirements. Farm diesel use is only about 3 percent of the total U.S. diesel market. The effect on the diesel fuel market would be negligible. Growing sunflower for fuel will exert downward pressure on oilseed meal prices.

Two million additional acres of sunflower would add 2 percent to the domestic oil meal market. However, oilseed meals are also exported, and domestic prices are closely related to the larger world market. Therefore, the affect of the projected increase in sunflower meal on the overall meal market would be very small. The effect on the sunflower oil meal market could be more consequential because different meals are not perfect substitutes for each other. Two million more acres of sunflower would result in 672,000 tons of 28 percent protein meal. Total sunflower meal production in 1982 was only 220,000 tons. A tripling of sunflower meal production would, in the short run, lower its price relative to soybean oil meal, its major competitor. However, the protein quality in sunflower meal is nearly as high as soybean meal. In 1982 the protein in 28-percent sunflower meal sold for 89 percent of the value of the protein in soybean meal. Being sunflower meal's overall nutritive value is 95 percent of soybean meal (Allen 1983), it is not likely sunflower meal prices would remain much below their present relation to soybean meal.

An estimate of the effects a sunflower-for-fuel program could have on business activity is illustrated using the budgets comparing sunflower production costs with acreage diversion for east central North Dakota. The per acre direct expenditures for sunflower production are \$51.36 greater than for diverted acres. When this expenditure is spent and respent throughout the economy, it results in an increase of \$131.00 per acre in gross business volume or a multiplier effect of 2.55 (Hertsgaard 1977). For example, if this program attracted 1 million acres in North Dakota in 1983, the total effect on the local economy would be approximately \$131,000,000 ($1,000,000 \times \$131/\text{acre}$). This assumes the expenditure difference for east central North Dakota would be

representative of the entire state. The above figures do not include the direct and secondary benefits to the local grain merchandisers, grain transportation system, and sunflower processors.

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PRODUCTION OF OILSEED CROPS AND VEGETABLE OIL FOR FUEL

IN THE PACIFIC NORTHWEST

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ABSTRACT

This paper presents the results of a study that assessed the economic feasibility of (1) growing oilseed crops in selected areas of Idaho and (2) of on-farm production and use of oil from the seeds as a diesel fuel substitute for farm machinery. In general, oilseeds are not as profitable as currently grown crops. The on-farm production and use of vegetable oil as a diesel fuel substitute further reduce farm income by \$0.57 - \$0.62 per liter of oil produced.

INTRODUCTION

Additional crops that could be grown economically in the inland Northwest would provide diversification of crop production and make better use of resources. Selected oilseed crops are adapted to these dryland areas and certain irrigated areas of the Pacific Northwest. Sunflower, safflower, and winter rape appear to be the most likely to have commercial significance. In addition, the potential of using the oil from these seeds as a diesel substitute is attractive because of recent shortages and greatly increased prices over the last five years. The objectives of this paper are (1) to determine the economic feasibility of producing and marketing oilseeds grown in the Pacific Northwest and (2) to assess the possibility of on-farm extraction of oil to use as an alternative fuel source for farm production.

Costs of Oilseed Production

Pacific Northwest agriculture is highly diverse due to climatic and geographical conditions. Irrigated areas can produce a wide variety of crops except where the growing season prohibits late maturing crop varieties. However, crops are much more limited in dryland areas, which include much of the inland Northwest. Dryland areas with low rainfall are limited to winter wheat and early maturing small grains and often use fallow to improve and increase crop production. Dryland farming in areas with 45 centimeters or more of precipitation can also produce peas and lentils as well as grain crops without fallow. Oilseeds are possible

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alternative crops for the region. In field trials, sunflower and safflower showed promise. Winter rape is also a possibility in areas with higher precipitation and mild winters.

The advantages of sunflower and safflower include drought tolerance, the ability to utilize farm equipment already available on grain farms, and harvest times that do not coincide with typical grain crops grown in the area. Winter rape also has these advantages and can utilize moisture well, as it is seeded in the late summer or early fall and is harvested the following summer.

A study in the late 1970's assessed the feasibility of growing oilseed crops on Pacific Northwest farms, especially on the dryland areas, but also on irrigated land. Production costs were evaluated and marketing possibilities were reviewed.

Early in the study, the second oil crisis resulted in fossil fuels being in short supply and prices rising considerably. The possibility of the use of vegetable oil as a substitute for diesel fuel was studied as a means of marketing the oil and as a possible substitute for diesel fuel in an emergency.

Table 1 gives production costs for selected crops and the price required for the sale of the crops to pay all expenses including land and property tax but excluding risk and management cost. With the possible exception of winter wheat, total production costs exceed prices received for the commodities. However, production costs include a value for the operator's labor and investment so his out-of-pocket costs may have been below the amounts received in the sale of the product. Oilseed crops usually compared fairly well with spring barley and peas in return per hectare of crops when selling for the market prices.

Figures 1 and 2 give prices that would need to be received for selected crops to make them equal to returns for winter wheat in Latah County and Power County, Idaho. Note that sunflower and safflower would need to be priced considerably above current market prices if they were to compete economically with winter wheat. On the other hand, the price of winter rape would need to rise only moderately to compete in price with winter wheat.

On-Farm Oil Production

A second major thrust of this project was to examine the economics of on-farm production and use of vegetable oils as diesel fuel substitutes. Concerns in the late 1970's and early 1980's over the price and availability of liquid fuels in farm regions created substantial interest in alternative sources of fuel and in on-farm methods of production. Much of the initial interest and research focused on alcohol production. Alcohol, however, cannot be readily substituted for diesel fuel, and since most energy intensive operations in field crop production are

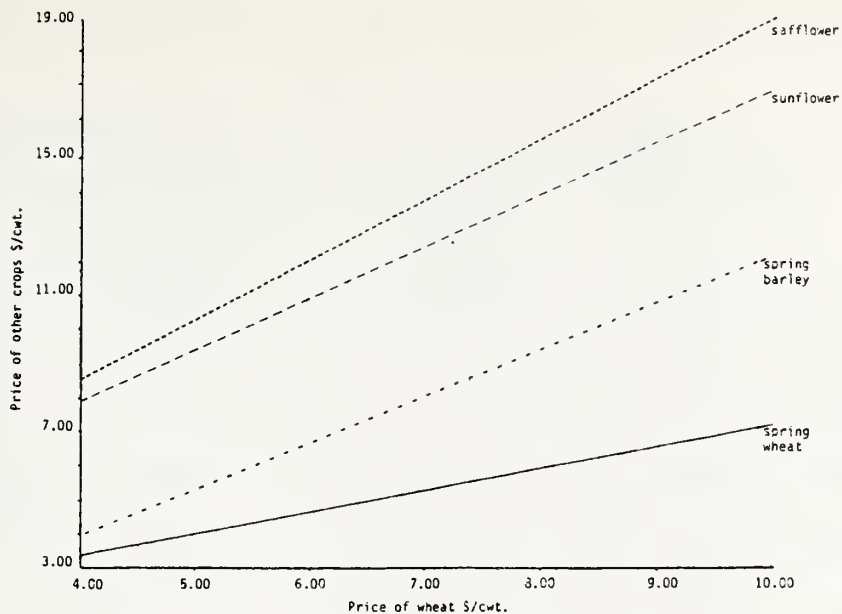


Figure 1. Estimated prices of other crops required to provide the same net income as winter wheat, Power County, Idaho, dryland.

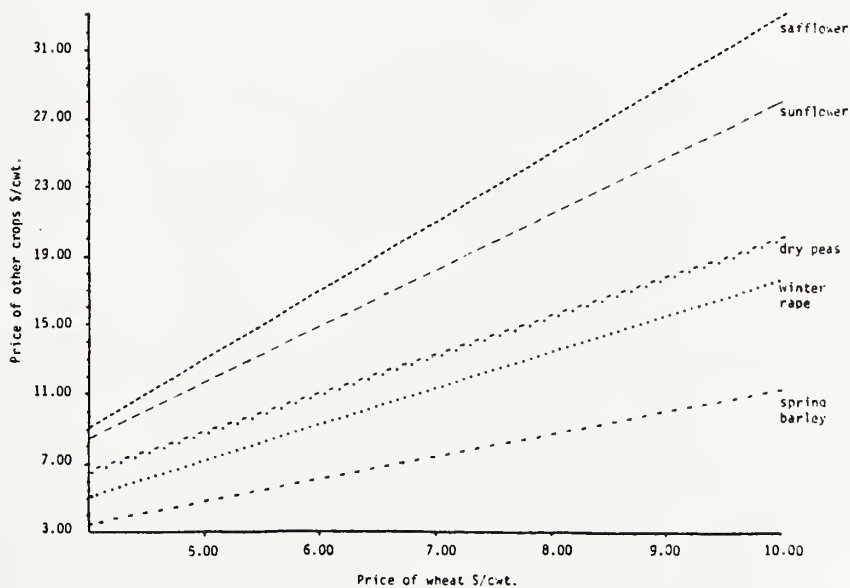


Figure 2. Estimated prices of other crops required to provide the same net income as winter wheat, northern Idaho, dryland.

Table I.--Production Cost per Hectare and Breakeven Prices for Selected Crops, Idaho, 1981

Crops	Latah County		Power County	
	Production Cost Per Hectare	Breakeven price per 100 kg.	Production Cost Per Hectare	Breakeven price per 100 kg.
Sunflower	\$449	\$33.28(15.13 /cwt.)	\$438	\$32.52(14.78 /cwt.)
Safflower	425	37.96(17.26 /cwt.)	407	36.36(16.52 /cwt.)
Winter rape	520	20.21(9.20 /cwt.)	--	--
Winter wheat	585	13.35(3.64 /bu.)	369	18.87(5.15 /cwt.)
Spring barley	438 /ton)	13.01(118	360 /ton)	16.01(145.60
Spring peas	469	24.56(11.16 /cwt.)	--	--
Spring Wheat	--	--	327	22.07(6.02 /bu.)

accomplished using diesel engines, it is necessary to develop a more suitable alternative to diesel oil.

Vegetable oils may provide that alternative. Engine tests indicate that vegetable oils are suitable substitutes for, and can be mixed successfully with, diesel fuel without greatly affecting power output or fuel consumption. These preliminary results, coupled with the fact that small scale oilseed-processing technology is much simpler and cheaper than alcohol distillation, led to the interest in developing oilseed crops as alternative sources of liquid fuel.

Linear programming models were constructed for Power and Latah Counties in Idaho to determine the economic feasibility of on-farm production and use of vegetable oils for fuel. The Latah County model determined a profit-maximizing solution that consisted of 223 hectares of winter wheat and 223 hectares of peas. Producing these crops required 25,130 liters of diesel and resulted in a gross margin of \$101,431.00. When the model was forced to produce vegetable oil for fuel, it chose winter rape as the most economical alternative. Producing winter rape oil reduced net income by \$0.62 per liter produced. When the model was forced to supply 100 percent of its fuel requirements from vegetable oil, the solution was 199 hectares of winter wheat, 99 hectares of peas, 31 hectares of winter rape, and 31 hectares of fallow. The fallow acreage appeared in this solution as a necessary condition of winter rape production. All of the rape produced was processed to provide 23,481 liters of fuel. The gross margin achieved fo

this combination was \$86,966.38, a 15-percent reduction from the original solution.

When the price of diesel was allowed to vary, the solution did not change until that price reached \$0.84 per liter. At this price, the same gross margin was achieved when all diesel was purchased as when all fuel was produced by growing and processing winter rape.

The Power County model determined the profit-maximizing solution to consist of 269 hectares of winter wheat, 269 hectares of spring barley, and 269 hectares of fallow. This combination resulted in a gross margin of \$70,866.67 and consumed 30,862 liters of diesel fuel. When this model was forced to produce vegetable oil for fuel it chose sunflower, which reduced net income by \$0.57 per liter produced. When the model was forced to supply 100 percent of its fuel requirements from vegetable oil, the profit-maximizing solution became 269 hectares winter wheat, 137 hectares of barley, 133 hectares of sunflower, and 269 hectares of fallow. All of the sunflower produced was processed to provide 31,646 liters of fuel. The gross margin achieved by this combination was \$52,712.47, a 26-percent reduction from the original solution.

When the price of diesel was allowed to vary, the original solution remained valid until the price of diesel reached \$0.85 per liter. At this price, the same gross margin was achieved when all diesel was purchased as when all fuel was produced by growing and processing sunflower.

Several key assumptions underlie the models. One is that the models utilize crop rotations. Therefore a solution implies that the rotations will be adhered to for the following seasons. Second, the models assumed vegetable oils to be perfect substitutes for diesel. A third major assumption was the ability of the farmer to process oilseed crops on a continuous, year round basis. The Latah County model required that the press be operated approximately 87 days for 12 hours per day, assuming a capacity of 41 kilograms per hour. The Power County model required operating the press 177 days for 12 hours per day, assuming the same capacity. The systems can, however, be automated to such a degree that hiring extra labor to operate the press should not be necessary. A further assumption is that the high protein meal by-product of oilseed processing is used as a livestock feed. This adds greatly to revenues. Sunflower and safflower meal are used successfully as livestock feeds. However, the meal from the variety of winter rape in this study is somewhat toxic to certain livestock and must be fed in reduced amounts and with great care.

SUMMARY

Oilseed crops are possible alternative crops in certain areas of the inland Northwest. However, the prices of oilseeds would have to be

considerably higher than current prices to yield the same net income as the traditional crops grown. This is particularly true of sunflower and safflower while winter rape is marginally competitive. Models were developed to test the economic feasibility of processing the oilseeds on-farm and using the oil as a diesel substitute in farm machinery. The results indicated that when diesel reached a price of \$0.84 - \$0.85 per liter (\$3.18 - \$3.21 per gallon), on-farm produced vegetable oil from winter rape in northern Idaho and sunflower in southeastern Idaho became a feasible alternative to diesel. At current prices, the income penalty from producing these oils was determined to be \$0.62 and \$0.57 per liter, respectively (\$2.34 and \$2.15 per gallon), for each area.

PROCESSING AND STORAGE

STABILITY STUDIES ON METHYL AND ETHYL FATTY ESTERS OF SUNFLOWER SEED OIL

L.M. Du Plessis and J.B.M. De Villiers^{1/}

ABSTRACT

Ethyl and methyl fatty acid esters of sunflowerseed oil were prepared on a laboratory scale by a method used for the large-scale preparation of fuel esters. Oxidative stability tests were performed on these esters with a Rancimat instrument. It was found that methyl esters had slightly longer induction periods than ethyl esters.

Tocopherol levels in esters were determined, and their anti-oxidant role is discussed. Food grade and technical grade tertiary butylhydroquinone were added to the esters, and it was found that these anti-oxidants increased the induction periods.

The results of this study can be used as practical guidelines for the storage of ester fuels.

INTRODUCTION

The composition, quality, and stability of sunflowerseed oil was previously studied in this laboratory (du Plessis 1982) to supply the local Division of Agricultural Engineering with specifications on the oil. The unmodified oil was used as a fuel for engine tests, and since it was shown that diesel engines with direct injection performed better on plant oil esters than on unmodified plant oil (Bruwer and Hugo 1981), long-term engine tests were undertaken with ester fuels (Hawkins and Fuls 1982). At that time, very little was known about the general stability characteristics and storage requirements of plant oil esters. Even less was known about the stability of esters made from different alcohols or from different oil types.

In this study, ethyl and methyl esters were prepared on a laboratory scale by a method used for the large-scale preparation of fuel esters (Fuls and Hugo 1981). Accelerated storage tests were performed, and induction periods for different esters were obtained. The efficiency of food grade and industrial grade tertiary butylhydroquinone and di-tertiary butylhydroquinone was also determined. Attention was given to the natural anti-oxidants, the tocopherols, which play a very important role in the protection of plant oils (Dugan 1980; Sonntag 1979).

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EXPERIMENTAL

Materials

Degummed sunflowerseed oil was supplied by Sentraal-Wes Coop., Viljoenskroon; methyl and ethyl alcohols, both A.R. and sodium hydroxide C.P. grade and silica gel 60 (particle size 0.063 - 0.20 mm) were supplied by E. Merck, Darmstadt; tertiary butylhydroquinone (TBHQ) of food and industrial grade, as well as 2,5 di-tertiary butylhydroquinone (Di-TBHQ), were supplied by Eastman Chemical International, Zug, Switzerland.

Methods

The catalyst (0.5% sodium hydroxide based on oil) was dissolved in the alcohol, added to the oil, and stirred at 50°C for about one hour. 1.6 Stoichiometric units of methyl alcohol and 2.0 stoichiometric units of ethyl alcohol were added to the oil. After esterification, the reaction mixture was transferred to a separating funnel where it was left for several hours at room temperature for optimum separation of the glycerol layer. After removal of the glycerol layer, the ester layer was washed with distilled water (ratio of water to esters 1:10). Moisture was removed by adding silica gel to the esters (5% w/w). The silica gel was then removed by careful shaking and filtration. Residual alcohol was removed under vacuum at 70°C.

The ash content of the esters was between 0.01 and 0.02%, and the sodium content, measured by atomic absorption spectroscopy, was less than 0.002%. The ester content of the samples, which was determined by gas chromatography, was in excess of 95%, and the moisture levels were less than 0.1% (Karl Fischer titration).

Esters were stored in closed glass containers at 5°C (light excluded) and, for comparison, similar clear glass containers were stored on the bench at room temperature (25 - 28°C).

Induction periods were determined on a Rancimat instrument (Zürcher 1974); TBHQ and tocopherol determinations have been described elsewhere (van Niekerk and du Plessis 1980; van Niekerk 1982).

RESULTS AND DISCUSSION

Induction Periods of Methyl and Ethyl Esters

Freshly prepared methyl esters had an induction period of 440 minutes, whereas a shorter induction period of 290 minutes was recorded for ethyl esters. This indicates that methyl esters are probably more stable than ethyl esters.

In this study, the esters were stored at room temperature in glass containers in indirect daylight, and the induction periods were determined at regular intervals over a period of 40 days. It was found that the induction periods of both methyl and ethyl esters decreased sharply during the first 16 days. After 16 days, the decrease was not so sharp and a baseline was reached (fig. 1). It is significant that the curve for ethyl esters was below that for methyl esters.

The induction periods of the esters that were stored in closed containers at 5°C were also determined. Under these conditions, the induction period was reduced by only 12.5% after 16 days as compared to a 60% reduction for the esters stored on the bench at room temperature (fig. 2).

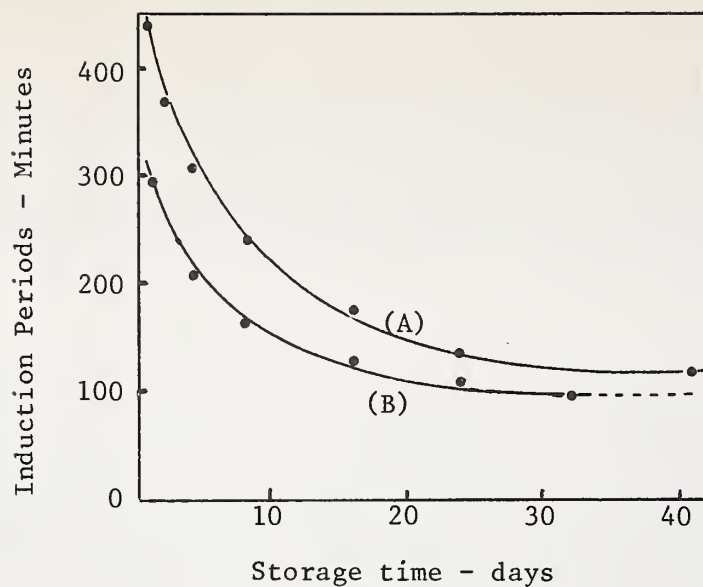


Fig. 1. Induction Periods of (A) Methyl and (B) Ethyl Esters stored at Room Temperature.

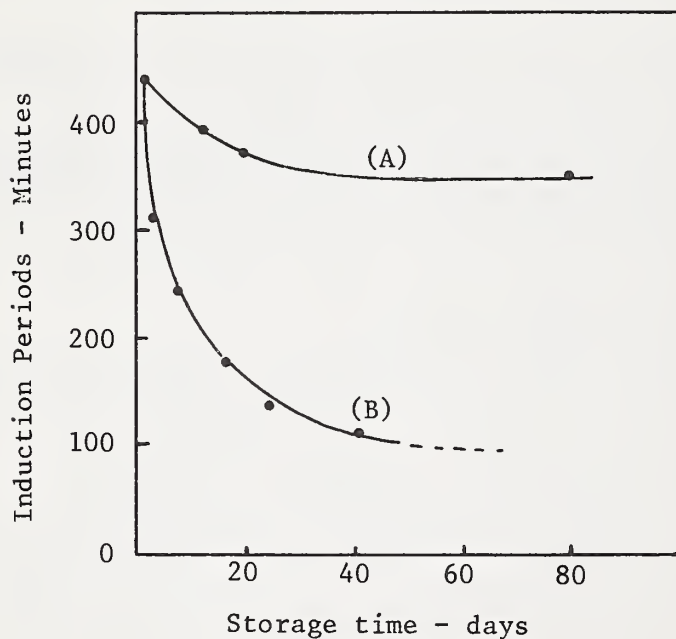


Fig. 2. Induction Periods of Methyl Esters stored at (A) 5°C and (B) at Room Temperature

Tocopherols in Esters

The esters studied so far contained no synthetic anti-oxidants--the tocopherols (natural anti-oxidants) in the esters had to be analysed.

Degummed sunflowerseed oil, which contained 68.1 mg tocopherols per 100 g, was used to prepare methyl esters, and it was found that the derived esters contained 49.0 mg tocopherols per 100 g (table I). The esterification process was therefore moderate enough to retain most of the tocopherols.

Sunflowerseed oil that was stored for 20 months contained 58.4 mg tocopherols per 100 g, and the derived methyl esters contained only 13.3 mg tocopherols per 100 g (table I). The induction periods of these esters were less than half those of the methyl esters previously mentioned (49.0 mg tocopherols/100 g).

Addition of Synthetic Anti-oxidants

The efficiency of TBHQ added to the esters was investigated. Three different types of TBHQ were studied, and the results for methyl esters are shown in figure 3. The food and industrial grade TBHQ had the same effect on the induction periods of the esters, and the optimum result had not yet been reached at the 0.3% addition level (fig. 3). Di-TBHQ was not as effective as TBHQ. The optimum level for di-TBHQ was approximately 0.3% (fig. 3). Addition of TBHQ at levels of 0.1% and 0.3%, therefore, increase the induction periods by 6.5 and 12 times, respectively.

TBHQ was also added (0.04% level) to sunflowerseed oil before esterification. The methyl ester prepared from that oil was further studied by comparing its induction period to that of esters prepared from oil that was not treated with TBHQ. The esters were again stored at room temperature in closed glass containers and the induction periods were determined at regular intervals over a period of 24 days. The results are illustrated in figure 4 where it is shown that the TBHQ-treated and untreated samples had about the same induction periods. However, after a four-day storage period, the TBHQ-treated sample performed slightly better than the untreated sample. The effect of TBHQ on the induction period was not as great as expected. Immediately after preparation of the esters, analysis showed only traces (less than 0.01 mg/100 g) of TBHQ. It was evident that the TBHQ was largely removed during the esterification process. This explains the weak performance of the TBHQ-treated sample.

CONCLUSIONS

Methyl esters of sunflowerseed oil had longer induction periods than ethyl esters, which indicates that methyl esters are probably more stable than ethyl esters.

When the esters were stored at room temperature, their induction periods decreased sharply during the first 16 days of storage, thereafter reaching a baseline. Storage at low temperature (5°C) resulted in a very small decrease in induction periods of the esters. It therefore appears that direct light and elevated temperatures are detrimental to the stability of the esters.

The esterification process is moderate enough to retain most of the tocopherols (natural anti-oxidants) in the derived esters. Small additions (0.1 - 0.3%) of synthetic anti-oxidants such as TBHQ to the esters increase their induction periods (stability) considerably. In pre-treated oils, however, the TBHQ is largely removed during the esterification process.

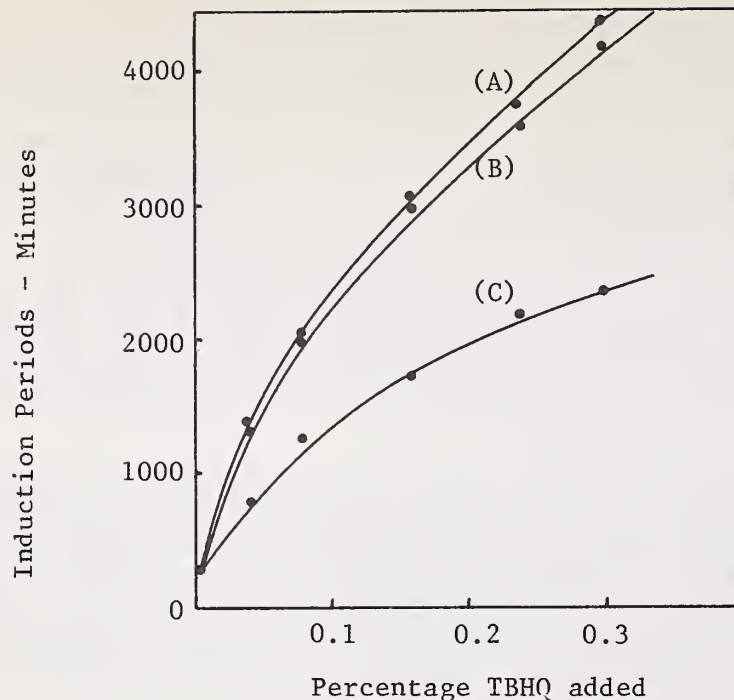


Fig. 3. Induction Periods of Methyl Esters Treated with TBHQ.
 (A) = Mono TBHQ (Industrial Grade)
 (B) = Mono TBHQ (Food Grade)
 (C) = 2,5 Di-TBHQ

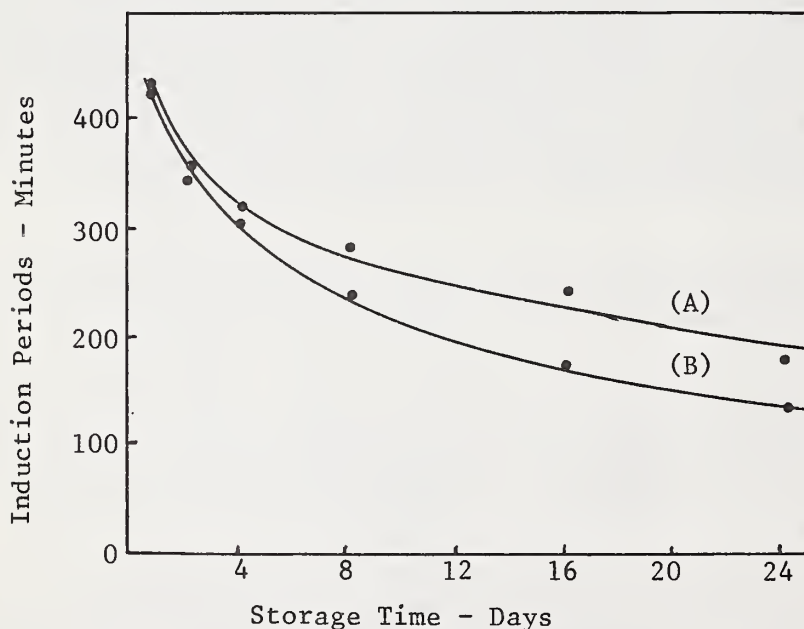


Fig. 4. Induction Periods of Methyl Esters Prepared from (A) 0.04% TBHQ-treated Oil and (B) Untreated Oil

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Table I.--Tocopherol content of sunflowerseed oil and esters prepared from the oil

Sample	Tocopherol content mg/100mg			
	α -t	γ -t	β -t	Total
A. Sunflowerseed oil (2 months old)	64.4	1.5	2.2	68.1
B. Methyl esters (from oil A)	45.7	1.2	2.1	49.0
C. Sunflowerseed oil (20 months old)	55.9	0.6	1.9	58.4
D. Methyl esters (from oil C)	11.2	0.4	1.7	13.3

EFFECT OF WATER QUALITY ON DEGUMMING AND STABILITY OF SOYBEAN OIL

H. A. M. Al-Kahtani, M. A. Hanna, and A. P. Handel^{1/}

ABSTRACT

Solvent extracted crude soybean oil was degummed with deionized distilled water containing various amounts of $\text{CaCO}_3\text{-MgCO}_3$, FeCl_2 , and NaCl . The total phosphorus content remaining in the degummed oil was determined, and the peroxide value of the degummed oil held at $98\text{-}101^\circ\text{C}$ was measured daily for 10 days. The results were compared statistically with those from oil degummed with deionized distilled water as a control. It was found that 250 mg/L of $\text{CaCO}_3\text{-MgCO}_3$ significantly reduced the efficiency of the degumming process. FeCl_2 at concentrations of 150 and 250 $\mu\text{g/L}$ and NaCl at 300 mg/L resulted in the removal of more phosphorus than the control at the 5-percent level of significance. Generally, the stability of the degummed oils decreased as the salt concentrations increased. The rate of oxidation was greater for oils degummed in the presence of FeCl_2 than of NaCl and $\text{CaCO}_3\text{-MgCO}_3$ under the same conditions.

INTRODUCTION

Degumming is a process by which 1-3 percent water with or without degumming agents such as phosphoric acid is mixed with crude oil at 300 to 500 rpm for 30 to 60 min at $60\text{ to }70^\circ\text{C}$ to render fat soluble impurities insoluble by hydration, which are then removed by centrifugation (Wiederman 1981). Carr (1976) reported that degumming removed 80 to 95 percent of the phosphorus present in soybean oil. Most of the hydratable phosphatides can be eliminated by degumming, but the nonhydratable phosphatides (Ca and Mg phosphatides) remain in the degummed oil. Letan and Yaron (1972) reported that the presence of Ca and Mg in crude and degummed oil prevented complete elimination of phosphatides by hydration.

There is no available information on FeCl_2 or NaCl solutions as degumming agents for degumming vegetable oils. However, it has been reported that phosphatides have the ability to form combinations with salts of various heavy metals. Tompsett (1934) indicated Fe^{+3} but not Fe^{+2} salts formed complexes with phosphatides. According to Thurman (1939), a 10-percent solution of NaCl aided the breaking of emulsions, and he recommended that NaCl solutions be used for washing phosphatides or precipitates because of its solvent action.

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The oxidation of lipids and oils and the decomposition of hydroperoxides are catalyzed by heavy metals, particularly those possessing two or more valency states (Fe^{+2} and Fe^{+3}) with a suitable oxidation-reduction between them (Schultz et al. 1962). According to List et al. (1978), FeCl_2 at concentrations of 0.1, 0.5, and 1.5 ppm significantly lowered the flavor stability of soybean oil. Alkali and alkali earth metals possess catalytic activity in oil oxidation due to induced hydroperoxide decomposition of free radicals (Ingold 1961).

There is an increased interest in the use of vegetable oil as a replacement for or extender of diesel fuel and an interest in processing the oil on the farm. The water used for degumming can be a factor in the quality of the final product. The purpose of this investigation was to study the effect of hardness of water (CaCO_3 and MgCO_3), FeCl_2 , and NaCl on the efficiency of degumming crude soybean oil. These degumming agents were used at concentrations in the range of those found in the groundwater of Nebraska. The concentration of CaCO_3 and MgCO_3 , Fe, and Na in the groundwater of eastern Nebraska, where soybeans are grown, exceeds 360 mg/L, 300 $\mu\text{g/L}$, and 50 mg/L, respectively (Engberg and Spalding 1978). NaCl concentration is relatively low, but it is important to know the effect of higher Na concentration when water is softened.

EXPERIMENTAL PROCEDURES

Sample Preparation and Degumming

Crude soybean oil was obtained from a commercial refiner. The CaCO_3 - MgCO_3 solutions were prepared with a ratio of Ca to Mg of 3 to 2. The crude oil samples were mixed with 1.5 percent of each solution as well as deionized distilled water (the control) individually. The mixtures were agitated mechanically at 400 rpm for 25 min at 60 C to hydrate the phosphatides and other colloidal impurities and then transferred to 250-ml bottles where the hydrated phosphatides and gums were separated by centrifugation at 4000xg for 15 min.

Total Phosphorus and Peroxide Value Determination

The phosphorus content of the crude and degummed oils were determined by the method of Racicot and Handel (1983). Degummed oil (100 ml) from each treatment was transferred to 120-ml glass jars (60 mm od x 70 mm) that were capped and stored at rest at 98-101 C. Peroxide value was determined daily on each sample in duplicate for 10 days (AOCS 1973).

Statistical Procedures

Significant differences between means were determined at the 5-percent level using Duncan's Multiple Range Test. Differences in slopes of regression lines were assessed to determine differences in the increase of peroxide values.

RESULTS AND DISCUSSION

Effect of CaCO_3 and MgCO_3 , FeCl_2 , and NaCl Solutions on Removal of Phosphorus During Degumming

Table I shows the percentage of phosphorus removed from soybean oil during degumming with 50, 150, and 250-mg/L solutions of CaCO_3 - MgCO_3 . The efficiency of the degumming process, when 250 mg/L was used, was lower than that with the control at the 5-percent level of significance. Ca and Mg reduced the efficiency of degumming process by leaving some of the phosphorus in the degummed oil. Non-hydratable Ca and Mg phosphatides were formed and depressed the hydration of the phospholipids in the crude soybean oil (Flider and Orthoefer 1981). The depression resulted from the competition between water and Ca and Mg for the same sites on the phospholipids. Hvolby (1971) reported that Ca and Mg reduced the hydration of the phospholipids by reducing the contact between the oil and the water phase.

Table I.--Effect of CaCO_3 and MgCO_3 , FeCl_2 , and NaCl Solutions on Phosphorus Removal from Crude Soybean Oil During Degumming

Sample	Phosphorus (ppm)	% Phosphorus
	remaining in degummed oil ^a	removal
Control	33.1 \pm 3.1	92.1
50 mg/L CaCO_3 + MgCO_3	35.4 \pm 4.0	91.6
150	35.4 \pm 1.4	91.6
250	42.1 \pm 1.9	90.0 ^b
50 $\mu\text{g/L}$ FeCl_2	38.5 \pm 3.9	90.9
150	26.2 \pm 3.5	93.8 ^b
250	28.3 \pm 4.0	93.3 ^b
100 mg/L NaCl	35.3 \pm 1.4	91.6
300	25.2 \pm 1.2	94.1 ^b
500	34.6 \pm 2.0	91.8

^aAverage of duplicate analyses on duplicate columns of two samples.

^bSignificantly different from the control at the 5-percent level.

The total phosphorus content of the degummed oil and phosphorus removed when 50, 150, and 250- $\mu\text{g/L}$ solutions of FeCl_2 were used is shown in table I. The higher concentrations of FeCl_2 resulted in the removal of more phosphorus than the control at the 5-percent level of significance. It is not clear why FeCl_2 might aid in removal of phosphorus compounds from crude soybean oil since the use of FeCl_2 solutions for degumming vegetable oils has not been reported. However, it has been reported that phosphatides can form a complex with various heavy metals. Tompsett

(1934) found that FeCl_3 formed insoluble complexes with phosphatides, which may explain the greater phosphorus removal in this study. In addition, FeCl_2 may also cause precipitation of phytic acid, which would also reduce the phosphorus content (Maga 1982). Phytic acid is a significant source of phosphorus in soybeans; however, it has not been reported to be present in crude soybean oil.

The effect of 100, 300, and 500-mg/L solutions of NaCl on the phosphorus removed from the crude soybean oil during the degumming process is shown in table I. The 300-mg/L concentration showed a significantly higher level of phosphorus removal during degumming than did the control. This confirms Thurman's (1939) report that NaCl was satisfactory for the purpose of precipitating phosphatides. In this study, there was poor separation at 500 mg/L as evidenced by a cloudy oil phase after centrifugation. The poor separation would lead to higher phosphorus values. The poor separation may be due to the formation of greater amounts of Na soaps at higher concentration. Beal et al. (1956) faced similar problems when using high concentration of NaOH for refining. They explained it by saying that there was unsatisfactory separation.

In conclusion, higher concentrations of $\text{CaCO}_3\text{-MgCO}_3$ (250 mg/L) reduced the efficiency of the degumming process significantly when compared to the control. In contrast, FeCl_2 at 150 and 250 $\mu\text{g/L}$ removed significantly more phosphorus than the control at the 5-percent level. A solution of 300 mg/L NaCl gave the most satisfactory results in removing more phosphorus than the control.

Effect of CaCO_3 and MgCO_3 , FeCl_2 , and NaCl Solutions On Degummed Oil Stability

The increase in peroxide values over time of the oil degummed with $\text{CaCO}_3\text{-MgCO}_3$ solutions is shown in figure 1. Linear regression effectively described the relationship between the peroxide value and time at the 5-percent level of significance for the control and 50, 150, and 250 mg/L $\text{CaCO}_3\text{-MgCO}_3$. The slope of each curve was compared to that of the control and there was no difference at the 5-percent level of significance.

It was expected that oil degummed with 250 mg/L $\text{CaCO}_3\text{-MgCO}_3$ would be more stable to oxidation because of greater amount of phosphorus remaining in the degummed oil. Lakshminarayana et al. (1982) reported that the development of oxidation as measured by peroxide value was faster in degummed oil than that of crude oil due to higher phosphorus content in crude oil. The expected stability caused by the higher level of phospholipids in degummed oil might have been balanced by an increased rate of oxidation due to $\text{CaCO}_3\text{-MgCO}_3$, which might have induced hydroperoxide decomposition of the free radicals. Ingold (1961) mentioned that the alkali and alkali earth metals possessed catalytic activity due to induced hydroperoxide decomposition of free radicals.

The peroxide values of the oils degummed with FeCl_2 solutions over the 10-day period are shown in figure 2. In general, these data show that the higher concentrations of FeCl_2 led to higher peroxide values.

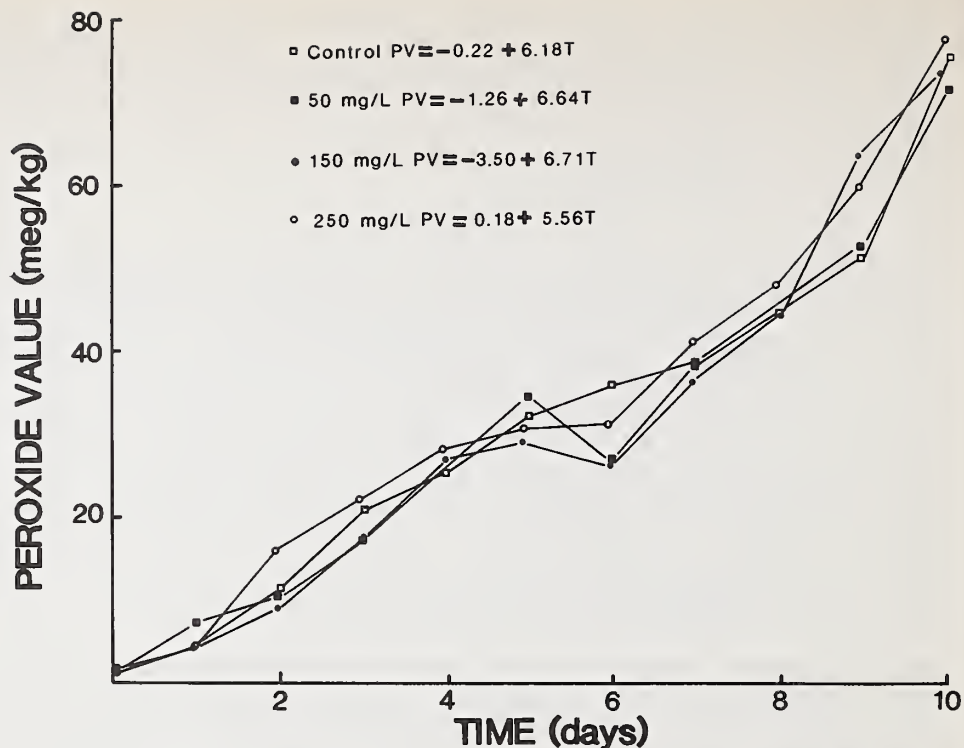


Figure 1.--Stability of soybean oil degummed with CaCO_3 and MgCO_3 solutions.

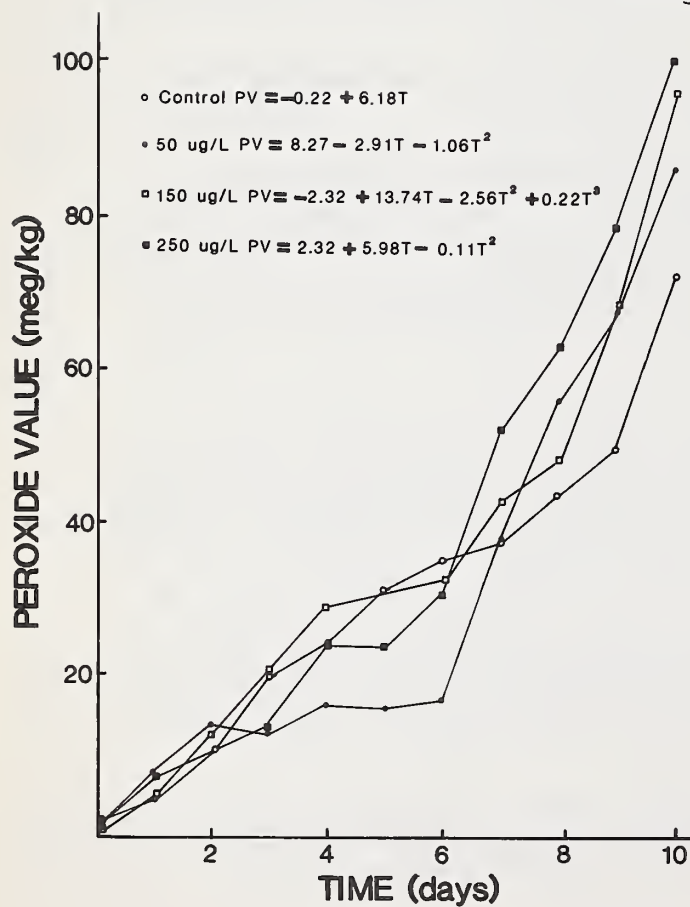


Figure 2.--Stability of soybean oil degummed with FeCl_2 solutions.

However, the relationship between FeCl_2 concentration and peroxide value changed as the concentration changed. For 50 and 250- $\mu\text{g/L}$ concentrations, a quadratic regression best described the relationship between the peroxide value of the degummed oil and time while cubic regression was best for 150 $\mu\text{g/L}$ FeCl_2 .

FeCl_2 has been shown to increase the rate of oxidative deterioration of degummed oil by reducing the length of the induction period, by increasing the rate of oxidation, and by affecting hydroperoxide decomposition (Schultz et al 1962). Since at 50, 150, and 250 $\mu\text{g/L}$ FeCl_2 the peroxide value was a quadratic or cubic function with time, the mechanism of oxidation was significantly different from that of the control whose regression was linear. This probably occurred because of the various reactions FeCl_2 affects during the initiation, propagation, and termination stages (Blanchard 1960).

The peroxide values of oils degummed with NaCl solutions over the 10-day period are given in figure 3. Higher concentrations of NaCl led to higher peroxide values compared to the control. Linear, cubic and quadratic regression described the oxidation with 100, 300, and 500-mg/L NaCl solutions, respectively. Since at 300 and 500 mg/L the peroxide values were cubic or quadratic functions, respectively, with time, the development and the mechanism of oxidation are significantly different from that of the control. However, Chang and Watts (1950) concluded that concentrations of NaCl below 5 percent inhibited the oxidation of lard and above 15 percent accelerated it. In this study, the oxidation of the oil degummed with 100 mg/L was lower than that of the control while higher for the oil degummed with 500 mg/L.

In conclusion, the oxidative stability of degummed oil decreased as the metal concentration increased. The development of oxidation was greater for FeCl_2 concentrations than for NaCl and CaCO_3 - MgCO_3 concentrations under the same conditions.

The authors recommend that, when degumming soybean oil, hard water with levels of CaCO_3 and MgCO_3 higher than 150 mg/L should not be used because of the undesirable effect of Ca and Mg on the effectiveness of the degumming process. In spite of the ability of high concentrations of FeCl_2 to remove more phosphorus during the degumming process, water with more than 100 $\mu\text{g/L}$ FeCl_2 should not be used because of its deleterious effect on the oxidative stability of the degummed oil. Finally, deionized distilled water or softened water with 300 mg/L NaCl should be used for degumming, depending on availability and cost.

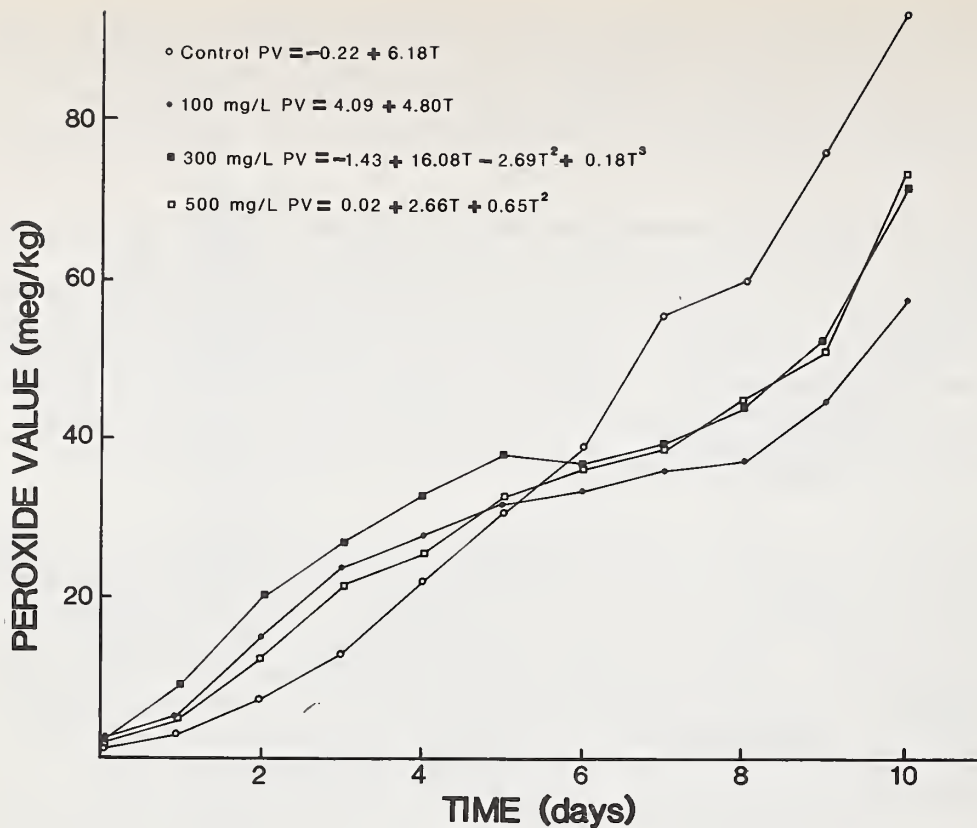


Figure 3.--Stability of soybean oil degummed with NaCl solutions.

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FUEL MODIFICATION

PARTIAL INTERESTERIFICATION OF PLANT OILS

C. R. Engler, L. A. Johnson, H. Jegasothy, M. B. Reddy, and C. M. Yarbrough^{1/}

ABSTRACT

Effects of varying reaction conditions on compositions of products from interesterification of sunflower oil with ethanol were evaluated. Optimum conditions for maximum conversion of oil to ethyl esters when using sodium ethoxide as catalyst were as follows: 1.8 times the theoretical amount of alcohol, room temperature, 0.8 percent catalyst (based on oil), and 2.5 hours. Increasing reaction temperature did not significantly reduce the time required to complete the reaction. The reaction was found to be extremely sensitive to moisture and free fatty acids, and required alkali refining and vacuum drying of crude sunflower oil to achieve acceptable results. Intermediate levels of conversion of sunflower oil to ethyl esters were obtained by varying the amount of ethanol from 0.33 to 1.8 times theoretical while keeping other reaction conditions constant.

Compositions of the reaction mixtures were determined by HPLC, using an Alltech C 18 column with methanol/2-propanol (3:1) as the mobile phase. The following standards were used to calibrate the system: alkali-refined sunflower oil, ethyl esters of sunflower oil, a mixture of monoglyceride standards in the same proportion as sunflower oil fatty acids, and four different diglyceride standards.

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David J. Hassett^{1/}

ABSTRACT

The University of North Dakota Engineering Experiment Station is currently engaged in research to investigate the chemistry, fuel performance, and economics of chemically modified sunflower oil for use as an emergency replacement diesel fuel. The idea of using vegetable oils as diesel fuels is an old one going back over 55 years to about the time when the diesel engine was invented. Current research on sunflower oil methyl ester formation represents one chemical approach to overcome the problems associated with the relatively high viscosity of sunflower oil when used as a diesel fuel replacement. Sunflower oil methyl ester has been prepared at the University of North Dakota Engineering Experiment Station. Physical and chemical properties of this fuel at varying levels of refinement were used to determine fuel properties. Engine testing carried out indicated that unrefined methyl ester, defined as at least 90 percent methyl ester with unreacted or partially reacted sunflower oil as the remainder, has about the same tendency to foul engines as Number 2 diesel fuel.

INTRODUCTION

Vegetable oils have been under consideration as diesel fuels for some time. Early work goes back to Gautier (1928) when vegetable oils were determined to be satisfactory diesel fuels. Aggarwal, et al. (1)^{2/} reviewed the work conducted in India, China, Japan, Great Britain, France, Belgium, West Africa, and elsewhere during the 1930's and 1940's. These studies determined that from purely technical considerations the use of vegetable oil as a diesel fuel is promising. There are a number of technical problems that require solutions.

Currently, much intensive research is ongoing, and the use of modified vegetable oil as diesel fuel has reduced or eliminated most of the problems reported earlier. These problems as described by Bruwer et al. (2) include injector fouling and sticking rings. The same study also concluded that ester formation has resolved these problems in a 100 hour-test when vegetable oils are used as fuels in direct injection diesel engines.

The process of alkaline transesterification of fatty glycerides has been described in early literature. The process as described by Trent (3) is essentially what we are currently using to prepare sunflower oil methyl ester. Results of this study indicate that a very satisfactory fuel is obtained by >90 percent conversion to methyl ester.

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^{2/}Numbers in parentheses refer to references at the end of the paper.

Our research has been directed toward answering the following questions on the formation of sunflower oil methyl ester to reduce fuel viscosity:

1. What is the optimal process of producing a 90 percent sunflower oil methyl ester diesel fuel with only viscosity reduction in mind?
2. How do these methyl esters perform in a diesel engine from the standpoint of fouling characteristics and engine performance, and what is the chemical makeup of an optimal methyl ester fuel?
3. What are the economics of the transesterification process on a production basis, and is it a viable process to attain a low viscosity fuel.

Sufficient other work has been done on actual engine performance with respect to power and fuel efficiency (5,6,7,8). These studies all seem to suggest the same things.

1. Vegetable oils foul injectors on direct injection engines and cause sticking of the rings. There is also a problem with vegetable oil that ends up in the crankcase polymerizing. All but the crankcase problem can be greatly minimized or eliminated by the use of engines with precombustion chambers.
2. The thermal efficiency of vegetable oil esters is slightly higher than petroleum-based diesel fuels.
3. Ester formation is a possible way to overcome all of the problems associated with vegetable oil diesel fuels, including the crankcase polymerization problems.

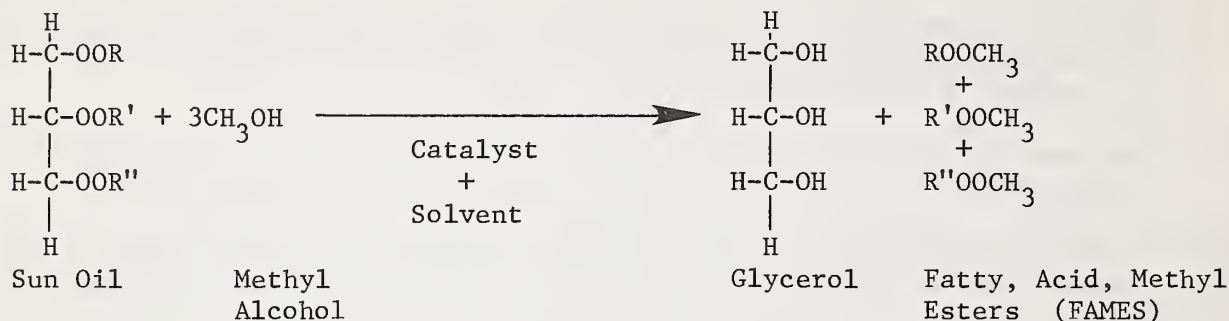
All raw oil and ester were characterized chemically. This characterization was done by gas chromatographic analysis and confirmed that the oil and ester were of the composition expected for sunflower oil from northern climates. In the future we feel it may be possible that this characterization, in addition to flash point and viscosity information, could be used as a means of checking vegetable oils and fuel grade esters before use or sale as diesel fuels.

The conversion of sunflower oil to sunflower oil methyl ester was accomplished by transesterification with methyl alcohol using sodium methoxide as a catalyst. 8.37 kg of sunflower oil (9L) was placed in a 12-L three-neck flask fitted with a reflux condenser, stirrer, and thermometer. The flask was heated with a jacketed heating mantle. As the oil was heating, but before it reached 40°C, 1456 g of methanol, which was reacted with 8.4 g of sodium, was added. The reaction mixture was stirred vigorously since sun oil and methanol are immiscible until ester formation begins. Methyl ester solubilizes the reactants. The reaction mixture was heated to 60°C and held there with stirring for two hours. The reaction mixture was then allowed to cool overnight without stirring. Two layers formed. The bottom layer, which consisted mostly of glycerol, was discarded and the top layer washed with water until the sodium catalyst residue was less than 2 mg/L. This washed layer was dried with anhydrous

sodium sulfate and used as fuel grade sunflower oil methyl ester.

In this synthesis, 5 moles of alcohol are used for each mole of vegetable oil instead of the 3 moles required. This excess is used to improve yield and aids in separation of the glycerol layer.

In this reaction:



R, R', and R'' are primarily 16 and 18 carbon chains. The triglycerides from the sun oil in this process are converted into three separate compounds, each a different methyl ester.

A portion of the fuel grade methyl ester was vacuum distilled to a refined methyl ester of about 100 percent purity. It was found to be unnecessary to use "refined" methyl ester, and in our work, it was used only for comparative data. It also gave us a full range of fuels, unreacted sunflower oil, fuel grade methyl ester, and "refined" methyl ester. Running the direct injection diesel engine on Number 2 diesel fuel and these three vegetable oil fuels has given us a better grasp of the relative performance of each of the alternative fuels. In an attempt to avoid difficulties due to catalyst inclusion (which is sodium for our synthesis), we included a washing step previously described to remove sodium. The ester was checked at intervals throughout the washing step to quantitate the catalyst residue until it was below two ppm sodium. This level was arrived at because it is the maximum level where distillation of fuel grade methyl ester to refined methyl ester is efficient, and the final product was not degraded during the distillation process by sodium. It is our intention to study the effect of sodium inclusion at different levels to discover whether the washing procedures may be reduced or perhaps eliminated. Reducing or eliminating the washing step would have a significant impact on the economics of the entire process.

ENGINE TESTING

Engine testing on chemically modified vegetable oils is being done on a Lister Model LT-1 direct injection diesel engine. This 5.25 H.P. engine is coupled to a 10 H.P. electric motor, wired so it can be used either as a starting motor or a dynamometer. Engine testing is done at constant RPM and constant loading since it has been found in our research and by others (9) that testing in this manner fouled engines in under 100 hours when pure vegetable oils were used. This allowed comparative testing to be done in a fairly short time and

with a minimum of fuel use.

It was noted during our work that both the fuel grade methyl ester and the refined methyl ester tend to form crystals at approximately 40°F. This is extremely unfortunate as farm work requires diesel engines to perform well below this temperature. A mechanical (i.e. fuel pre-heating) rather than chemical solution to this situation would seem more practical at this point.

ETHYL ESTER

The success of our research on sunflower oil methyl ester as a replacement diesel fuel has prompted ideas for complimentary research on chemically modified vegetable oils. In our case at the University of North Dakota, sunflower oil is still the obvious choice since sunflowers are a major crop in this area, however, our research is applicable to a group of oleic - linoleic oils among which are sunflower, cottonseed, peanut, corn, safflower, olive, and palm. Primary research goals and objectives are:

1. Utilizing renewable resources
2. Improving fuel low-temperature properties
3. Developing fuel specifications that are applicable to vegetable oil fuels

The use of ethyl ester is a step toward a totally renewable fuel and at the same time offers a slight improvement in fuel low-temperature properties. Methyl ester forms crystals at about 40-45°F while ethyl ester is suitable for fuel use to about 30-35°F. It is expected that engine testing, when completed, will demonstrate that ethyl ester performs as well as methyl ester from a fouling standpoint.

Raw Material Cost for 1,000 gallons

Sun Oil Ester

Methyl Ester		Ethyl Ester	
7,217 lb sun oil	-	7,217 lb sun oil	-
193 gal methyl		277 gal ethyl	
alcohol	\$ 156	alcohol	\$ 504
75 lb catalyst	46	75 lb catalyst	46

Although this comparison shows that ethyl ester when prepared with a 1.6 molar excess of alcohol as previously described for methyl ester is more expensive, the percentage increase when the cost of sunflower oil is included is not that great. Ethyl ester is of great interest in North Dakota where large ethanol production facilities are currently being developed.

OZONOLYSIS

Ozonolysis as a means to improve low-temperature properties of sunflower oil methyl ester is currently under investigation. Ozone can be used to cleave double bonds with subsequent formation of acids or aldehydes, depending on whether oxidative or reductive work-up of reaction products is followed. The ozonolysis of oleic acid with possible reaction products is as follows: (10)

chromatographic analysis of fatty acids. Since distillation of glycerides or fatty acid esters at atmospheric pressure causes decomposition, and vacuum distillations are difficult to run and duplicate, a chemical analysis by fatty acid composition could substitute and would provide virtually the same information.

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ESTERS FROM RAPESEED OIL AS DIESEL FUEL

M. J. Nye and P. H. Southwell^{1/}

ABSTRACT

Convenient room temperature conditions for the synthesis of methyl and ethyl esters from rapeseed oil have been found. Reaction conditions and physical properties are reported.

INTRODUCTION

Stimulated by rising prices of mineral oil, research into vegetable oils as substitutes for diesel oil was rejuvenated after several decades of disinterest. Vegetable oils are effective diesel substitutes, but their high viscosities relative to diesel oil give rise to poor atomisation leading to engine and injector deposits and also injector pump failure. Workers in South Africa initiated studies of methyl and ethyl esters derived by transesterification of sunflower oil in the presence of methanol or ethanol, since these materials are much less viscous than their parents (1. Fuls and Hugo, 1981). These researchers and other groups (references 2,3,4,5,6) have shown that methyl and ethyl esters of various vegetable oils are indeed effective diesel oil substitutes and because of their lower viscosity appear to be superior to the parent vegetable oils. Regarding rapeseed oil, another group in Saskatchewan (7. Strayer, Craig, and Zoerb, 1982) beside ourselves (8. Nye, Southwell, 1981) is active.

In this present study, conditions for the synthesis of ethyl and methyl esters from rapeseed oil at room temperature were developed. The fuels were subjected to short-term engine tests, using a one-cylinder diesel engine, and the results of these tests will be briefly mentioned in this paper.

EXPERIMENTAL

Materials

The rapeseed oil supplied by Maple Leaf Mills had been obtained by simple crushing and filtering of the seed and had not been washed. Alcohols were dry spectrograde and were stored over molecular sieves (Linde 4A). Catalysts were reagent grade.

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Methods

Transesterification reactions were mostly conducted on the small scale by stirring the reaction mixture in a 250-cc flat-bottomed conical flask with a magnetic stirrer (Fisher Thermax Model 210T), using a one-inch stirring bar. A CaCl_2 drying tube was attached. The temperature was controlled by immersing the flask in a thermostatted water bath. The reactions were usually quenched with water plus a little dilute HCl to make the pH slightly acidic.

The approximate percentage of methyl ester formed during transesterification was determined by proton n.m.r., using the methyl peak. More accurate ester concentrations were determined by gas chromatography, usually using a Varian model 370 instrument with a silicone (5-pct SE30 on chromosorb W, 6' x 1/8") column, flame ionization detector, and applying esters of heptadecanoic acid as internal standards. Soap concentrations were determined by back titrating the quenched fuel with standard alkali and following potentiometrically. The amount of soap is indicated by the amount of alkali required to titrate from one inflection point to the other.

The 25-litre scale synthesis of ester fuels was conducted in an enclosed stainless steel cylindrical drum stirred by a 4-dm diameter propeller driven by a 1/3-horsepower electric motor.

RESULTS AND DISCUSSION

Temperature

An important objective of this work was to find out whether esters could be conveniently synthesized at room temperature, and although many of the experimental conditions tried required elevated temperatures to effect reaction, eventually successful conditions at room temperature were found by systematically optimizing the variables. The main variables are catalyst, catalyst concentration, rapeseed oil/alcohol ratio, and stirring rate.

Catalyst

The following types of catalysts were tried: magnesium and calcium oxides and carbonates, basic and acidic macroreticular organic resins, alkaline alumina, sodium and potassium hydroxides and alkoxides, phase transfer catalysts, sulfuric acid, p-toluenesulfonic acid, and dehydrating agents as co-catalysts. The only catalysts found to be effective at room temperature were the alkoxides and hydroxides. The effect of concentration of catalyst on the yield of methyl or ethyl ester was measured under various conditions, and a representative result is shown in figure 1, which gives the relationship between percentage yield of ethyl ester and concentration of NaOH for various reaction times. It can be seen that 1-percent NaOH is an effective catalyst at room temperature if a 60-minute reaction time is allowed. Methyl ester formation and the alkoxides catalysts show similar behaviour. NaOH was chosen as the preferred catalyst because of its lesser cost, and 1 percent was the chosen concentration.

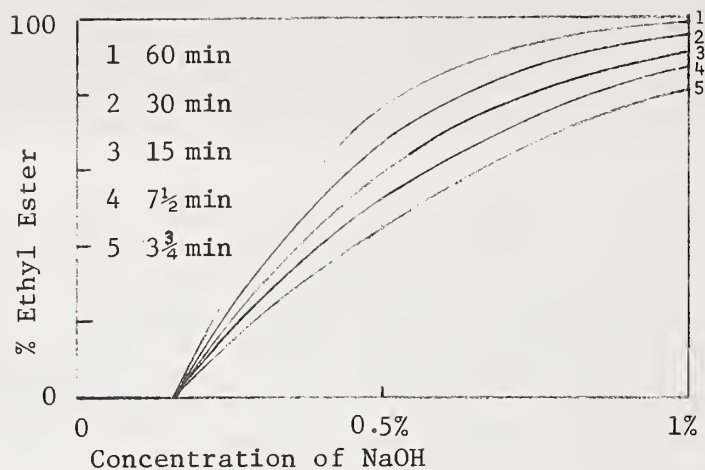


Figure 1.--Percentage of ethyl ester versus concentration of NaOH for various time intervals at 24°.

Soap can be a substantial by-product and, if all of the 1-percent NaOH is converted to soap, the result is a decrease in overall yield of ester by 7.3 percent. In reality, 4- or 5-percent loss is observed. However, if higher concentrations of alkali are used, the production of soap becomes progressively more dominant. Similarly, contamination by water increases the yield of soap, but we found that this was not a problem if the presence of water was below 1 percent.

Ratio of Alcohol to Rapeseed Oil

In a study of methanol transesterification of sunflower oil (9. Freedman and Pryde 1982), it was shown that unless at least six moles of alcohol per mole vegetable oil are used, the final product will contain appreciable amounts of mono-, di-, and tri-glycerides. Thin layer chromatographic analysis of products showed this also to be the case in the present work, and so the 6:1 ratio was chosen as the preferred condition. In this way, glyceride concentration can be kept low if the degree of reaction is kept high. The 6:1 ratio also has the advantage that the rate of reaction is at maximum at that ratio as shown in figure 2.

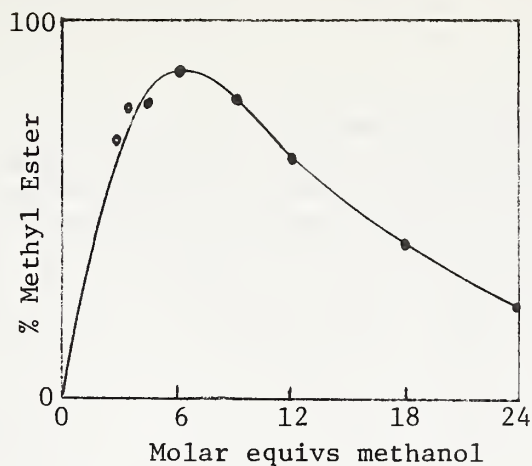


Figure 2.--Percentage of methyl ester versus molar equivalents of methanol (1% NaOH, 24°, 20 minutes).

Stirring Rate

Since the reaction mixture comprises two phases, it was not surprising to find that the rate of reaction was profoundly controlled by the rate of agitation. Figure 3 shows the relationship between relative rate of reaction and dial setting on the magnetic stirrer. In practice it was

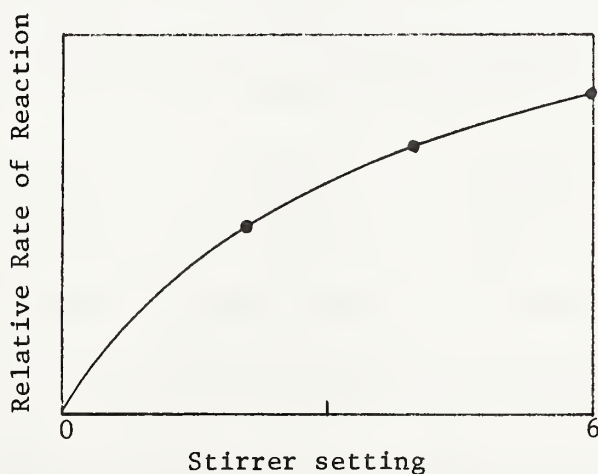


Figure 3.--Rate of methyl transesterification versus stirrer setting.

found that that rate of reaction was satisfactory if the stirring action was vigorous and there was some splashing. The same criterion was found to apply at the 25-litre scale. Simple swirling action was not satisfactory.

SYNTHESIS OF FUEL

Based on the above studies, the conditions for synthesis of either ethyl or ethyl esters from rapeseed oil were as follows. The reaction solution was a mixture of crude rapeseed oil plus a solution of 1% NaOH (weight relative to weight of oil) dissolved in 6 molar equivalents of dry methanol or ethanol. The solution was stirred with splashing for one hour at 24°C. It was then washed with a volume of water equal to half the volume of oil, three times. The oil was dried over anhydrous CaCl₂ and filtered to remove fine particles.

PROPERTIES

Table I lists some properties of the ester fuels.

Table 1.--Characteristics of ester fuels

Property	Methyl Fuel	Ethyl Fuel	Diesel oil	Units
Percentage ester	92	95	-	pct
Viscosity	4.4	4.4	2.2	Cps 40°C
Flash point	177	185	>52	°C
Cetane number	49.6	53.5	>40	
Physical characteristics at 5°C	liquid	liquid	liquid	
-5°C	1/4 solid	liquid	liquid	
-15°C	solid	mostly solid	liquid	

It can be seen that the cetane numbers and flash points are good relative to diesel oil, but low temperature properties are poor. Viscosities are far closer to that of diesel oil than rapeseed oil (34 Cps 40°C).

CONCLUSIONS

A method for converting rapeseed oil to ethyl or methyl esters at room temperature has been developed. Only simple equipment and techniques are used, and the method is suitable for on-farm application. Short-term tests have been carried out on the fuels by Professor P.H. Southwell, School of Engineering, University of Guelph, and the esters were found to be similar to rapeseed oil with respect to power and fuel consumption, and superior to rapeseed oil with respect to exhaust particulates. Inspection of cylinders, piston rings, and injectors was made, but longer term tests would be required before drawing any definite comparisons.

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COMMERCIALIZATION OF ESTER-BASED DIESEL FUEL FROM VEGETABLE OILS

M. D. Webster and S. S. Fine^{1/}

Globus Resources Ltd. and its affiliated company, United Guardian, Inc., have developed and tested a commercial process for the production of Dieselite (a methyl ester based diesel fuel extender) and chemical co-products, from vegetable oils. An extensive program of static and dynamic engine tests has shown performance of coconut oil-derived Dieselite blends in unmodified diesel engines to be fully equivalent to conventional diesel fuel with the advantage of greatly reduced particulate exhaust emissions. This paper discusses the commercial, technical, and other aspects of this program.

¹Webster and Fine are from United Guardian, Inc., New York, N.Y.

VEGETABLE OIL METHANOL SYSTEMS AS FUELS FOR DIESEL ENGINES

A. W. Schwab and E. H. Pryde^{1/}

ABSTRACT

Vegetable oil methanol fuels have been developed for possible use in diesel engines. These fuels are clear, thermodynamically stable liquid systems with viscosities near the ASTM specified range for #2 diesel fuel. They are micellar systems and may be formulated ionically or nonionically. Either method spontaneously microemulsifies methanol and vegetable oils into clear homogeneous systems that otherwise would separate into two phases. Nonionic systems utilize 2-octanol or other long-chain fatty alcohols whereas ionic systems use triethylamine soyate to achieve miscibility.

INTRODUCTION

Currently, methanol and ethanol are receiving considerable attention for use in both spark and compression ignition vehicles. At Seminar II, attention was focused on vegetable oils as fuels for diesel engines. At that seminar it was disclosed that the viscosity problem associated with vegetable oils could be eliminated by microemulsification, and formulations for triglyceride-aqueous ethanol microemulsions were disclosed. Since Seminar II, our attention has been directed toward vegetable oil-methanol systems. Two hybrid fuel systems have been formulated to meet viscosity and cetane number requirements for a #2 diesel fuel replacement.

DISCUSSION

Triglyceride-methanol microemulsion systems are attractive from an economic as well as a renewable resource viewpoint. Methanol has an advantage over ethanol, because it can be derived from a large variety of base stocks. These include biomass, municipal waste, natural gas being flared at refineries and from coal. Technical problems, however, must be solved before triglyceride-methanol systems can be used in diesel engines. One problem is that of phase separation, and a second is the viscosity problem inherent with vegetable oils. Both obstacles can be overcome by microemulsification. Microemulsions of methanol in triglycerides are clear, thermodynamically stable liquid fuels with viscosities near the upper ASTM specified range (4cSt @ 37.8°C) for #2 diesel fuel. These are micellar systems and may be formulated ionically or nonionically. Ionic systems use triethylamine soyate whereas nonionic systems utilize 2-octanol or other long-chain fatty alcohols to achieve miscibility.

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Ternary Phase Diagrams

Figure 1 is a ternary or phase equilibrium diagram for the system: triolein/2-octanol/methanol. Determinations were made at 25°C of the limiting solubility and the tie lines in the ternary system according to customary procedures. This figure establishes the solubility of methanol in triolein at 25°C using 2-octanol as the solubilizing agent. 2-Octanol (sec-caprylic alcohol) is currently available in large surplus as a byproduct obtained by high-temperature caustic oxidation, under pressure, of castor oil (a renewable resource agricultural product). Point A shows location of fuel #1 (53.3% SBO, 33.3% 2-octanol and 13.4% methanol).

Figure 2 is a ternary diagram for the system: triolein/triethylamine soyate/methanol and establishes the solubility of methanol in triolein at 25°C using triethylamine soyate (soap of triethylamine and soybean oil fatty acids) as the solubilizing agent. Point P on both Figures 1 and 2 shows the plait point for each system.

Viscosity

Figure 3 is a viscosity curve for a 2/1 volume ratio of soybean oil to methanol, which is solubilized by added amounts of 2-octanol. Viscosity decreases rapidly with increasing amounts of 2-octanol and, at approximately a 30 percent volume concentration of 2-octanol, the hybrid fuel has a viscosity near the upper ASTM limit specified for #2 diesel fuel. Other ratios of soybean oil to methanol have been studied and are shown in Figure 4 along with other solubilizing agents.

Cetane Numbers

Cetane number, a measure of the ignition quality of a diesel fuel, depends primarily on the chemical composition of the fuel. ASTM specifies a minimum cetane number of 40 for a #2 grade diesel fuel. High-cetane fuels permit an easier engine start, provide quick engine warm-up, reduce engine knock and give minimal carbon and varnish deposits. Unfortunately, methanol and ethanol have no or very low cetane numbers, although their combustion does provide energy for the diesel engine. Triglyceride oils have cetane numbers close to the minimum specified ASTM range for #2 diesel fuel. Table I furnishes data on cetane numbers of components of some hybrid fuels. 2-Octanol with a cetane number of ≈ 30 is close to the range for some #2 diesel fuel substitutes. Oleyl alcohol has the highest cetane number of the alkanols studied and would be the preferred one except that it is also the most expensive alcohol. The calculated cetane value for hybrid fuel #2 was made assuming a cetane number of unity for methanol.

Costs

Based upon prices of soybean oil, 2-octanol, and methanol at 17¢, 35¢, and 12¢ per pound, respectively, the cost of hybrid fuel #1 would be approximately \$1.50 per gallon. At prices of 24¢, 35¢, and 7¢ per pound, respectively, the cost of hybrid fuel #1 would be approximately \$1.70 per gallon.

TABLE I.--Cetane numbers

Sample	Cetane Number (ASTM D-613)
Oleyl alcohol	60.0
2-Octanol	30.1
2-Ethyl-1-hexanol	<4.0
Soybean oil	37.9
Hybrid fuel #1 (53.3% SBO, 33.3% 2-octanol, 13.4% CH ₃ OH)	31.4
Hybrid Fuel #1 (+0.5% hexyl nitrate)	34.1
Hybrid Fuel #1 (+2.0% hexyl nitrate)	36.0
Hybrid fuel #2 (53.3% SBO, 33.3% oleyl alcohol, 13.4% CH ₃ OH)	(40.2 est'd.)

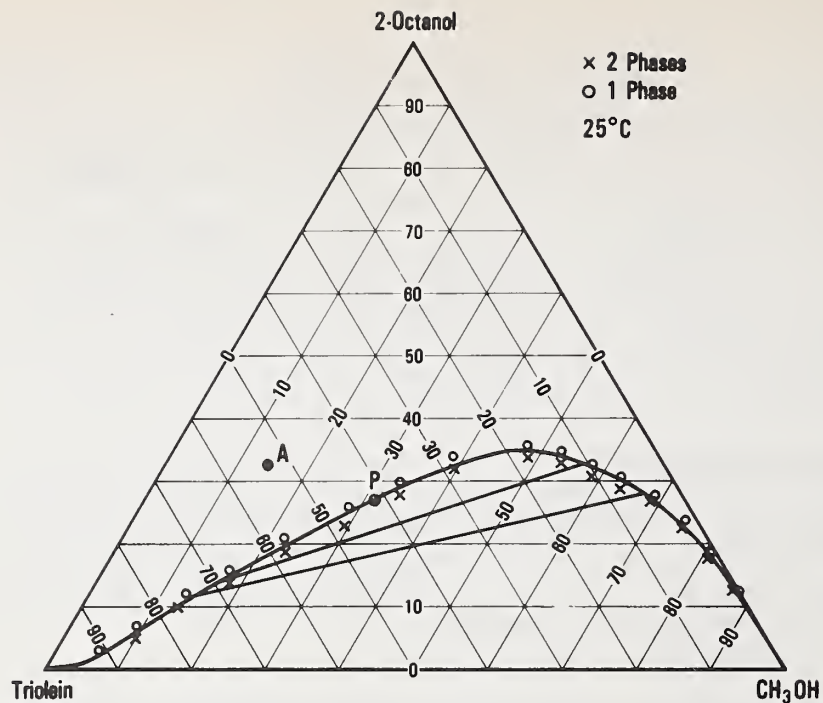


Figure 1.--Ternary phase equilibrium diagram for triolein, methanol, and 2-octanol at 25°C.

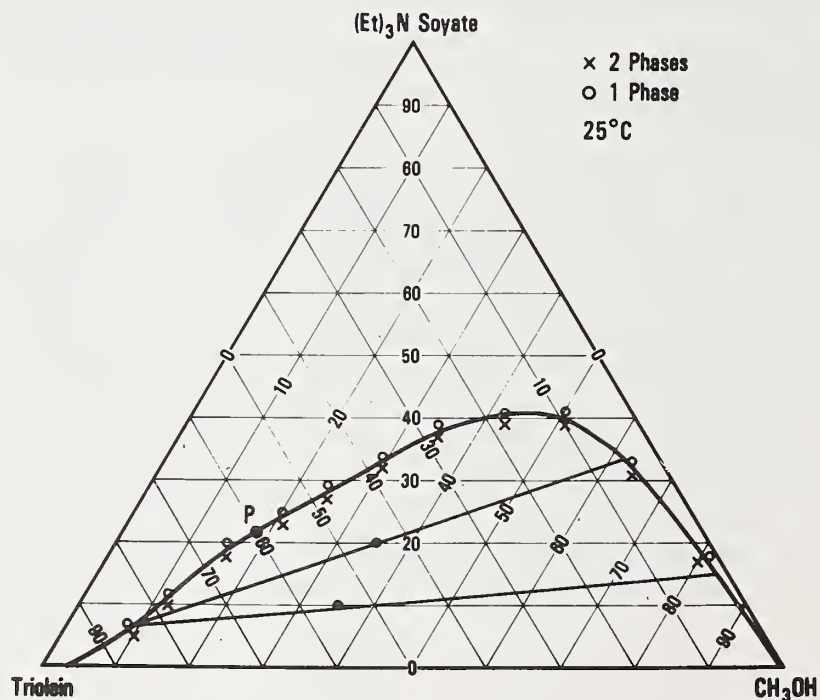


Figure 2.--Ternary phase equilibrium diagram for triolein, methanol, and triethylamine soyate at 25°C.

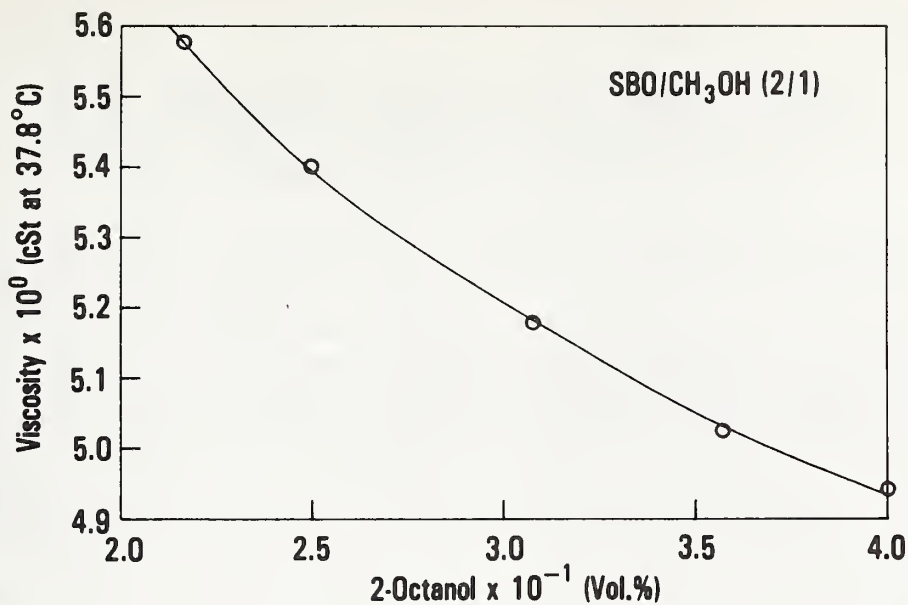


Figure 3.--Kinematic viscosities at 37.8°C for 2/1 volume ratios of soybean oil/methanol with added 2-octanol.

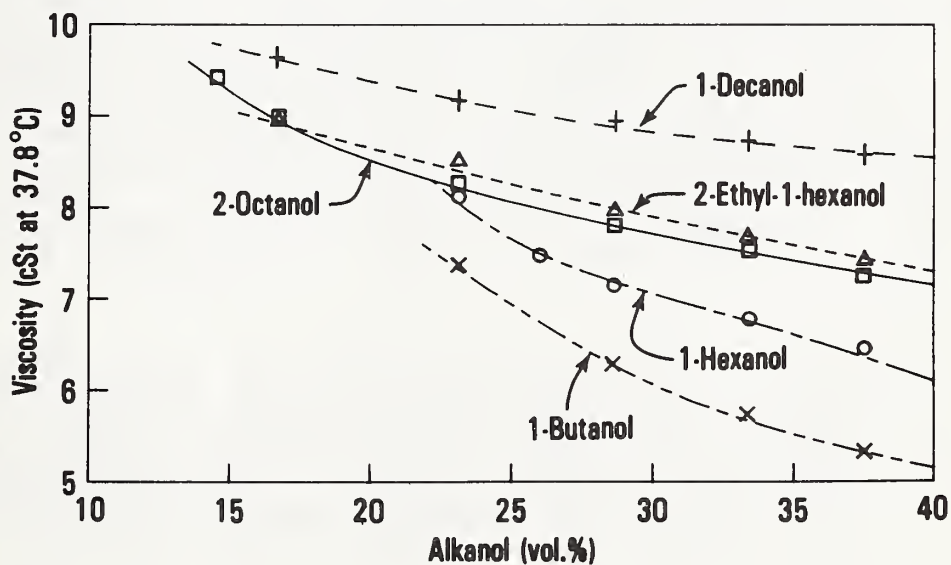


Figure 4.--Kinematic viscosities at 37.8°C for 4/1 volume ratios of soybean oil/methanol with C₄ to C₁₀ alcohols.

COOPERATIVE WORK ON ENGINE EVALUATION OF HYBRID FUELS

E. H. Pryde and A. W. Schwab^{1/}

ABSTRACT

At our present state of knowledge, vegetable oil methyl or ethyl esters appear to be the best approach for emergency use in direct-injection diesel engines. Considerably more long-term endurance tests in a variety of engine models and designs will be needed before engine manufacturers will support warranties with such fuels. Long-term endurance tests are also needed to test the promise that vegetable oil microemulsion fuels seem to have. In the meantime, research needs to be continued to develop basic information on the kinetics of transesterification, on thermodynamic properties of both ester and vegetable oil hybrid fuels, and on the properties of new vegetable oil microemulsions.

INTRODUCTION

Vegetable oils are liquids from renewable resources, have 88 percent of the heat content of diesel oil (Goering et al. 1982b), and apparently have good potential as alternative fuels to help maintain crop production during fuel shortages. In reality, vegetable oils cause a number of problems when used in direct-injection diesel engines. The problems can be traced to the high viscosity, extremely low volatility, and polyunsaturated character of vegetable oils, the former two properties leading to improper injection and atomization and the latter resulting in formation of crosslinked gels and carbon residues. Vegetable oils do have several favorable attributes, which make worthwhile the research and development necessary to show how they might be used. For example, they have favorable energy output/input ratios on the order of 2 to 4:1 for nonirrigated crops (Goering and Daugherty 1982).

Engine design is a major factor in the successful use of vegetable oils as alternative fuels. An indirect-injection, air-cooled, naturally aspirated engine has been shown to operate more than 2300 hr on 100 percent sunflower oil (du Plessis 1981). Older engines having precombustion chambers operated successfully with vegetable oils after World War I and during World War II. In contrast, a number of diesel engines, having a direct-injection feature

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in common, have been shown to be incompatible with 100 percent sunflower oil; a 20-percent blend of sunflower oil in diesel oil is about the maximum concentration that can be tolerated (Bruwer et al. 1981). Since by far the majority of farm tractors in the U.S. are powered by the more fuel efficient direct-injection engine (compared to the indirect-injection engine), and since the cost of modifying the engines would be prohibitive, the major emphasis in recent investigations has been in modifying the fuel. At least three major proposals have been made to alleviate the problems associated with the use of vegetable oils as fuel:

- Heat the fuel to temperatures sufficient to bring the viscosity to near specification range. At 145°C, the viscosity of vegetable oils is about 4.0 cST (Ryan et al. 1983).
- Convert the vegetable oil to the simple esters of methyl, ethyl, or butyl alcohols. Results to date indicate that the esters are superior diesel fuels for direct-injection engines (Hawkins and Fuls 1982).
- Dilute vegetable oil with other materials to bring the viscosity to near specifications.

This paper reviews engine test results obtained with microemulsions, with simple esters of vegetable oils, and with certain vegetable oil-diesel oil blends.

DISCUSSION

Microemulsions

Hybrid fuels of special interest are water-in-oil type microemulsions in which the vegetable oil is the continuous phase and aqueous ethanol forms the dispersed phase (Schwab et al. 1983). (table I).

Table I.--Composition of the Hybrid Fuels, Volume Percent
=====

Fuel component	Hybrid fuel		
	Ionic	Nonionic	Diesel-nonionic
Diesel oil	0	0	50
Soybean oil	52.3	53.3	25
190-Proof ethanol	17.4	13.3	5
1 Butanol	20.5	33.4	20
Linoleic acid	6.54	0	0
Triethyl amine	3.27	0	0

=====

Engine Performance Tests

The hybrid fuels performed better than might be expected from their fuel properties (table II). (The ionic microemulsion has not been tested in an

engine as yet). The low cetane numbers of the hybrid fuels had no adverse affect on their short-term performances in the engine. Analysis of the engine test results gave the following conclusions (Goering et al. 1982a):

- The nonionic microemulsion produced nearly as much engine power as No. 2 diesel fuel, despite having a 19 percent lower heating value.
- The nonionic fuel gave slightly higher thermal efficiency, higher engine power, and lower specific fuel consumption than the ionic hybrid, and thus was slightly more effective as a fuel.
- The microemulsions gave lower exhaust temperatures, reduced exhaust smoke, and lower carbon monoxide and nitrogen oxide emissions than noted with No. 2 diesel fuel.
- The hybrid fuels were less volatile than ethanol and thus could be handled safely with procedures considered safe for ethanol.

Table II.--Fuel Properties of Hybrid Fuels

Property	Hybrid fuel		
	Ionic	Nonionic	Diesel-nonionic
Viscosity, mm/s ² , 37.8°C	8.77	6.77	3.69
High heat value, KJ/kg	36,687	37,045	41,263
Cetane no.	29.8	25.1	38 (est.)
C/H Ratio	--	4.99	5.83
Air/Fuel ratio	11.6	11.5	13.1
Flashpoint, °C	22.2	27.8	38

Heat-release patterns indicated that the hybrid fuels burned faster than diesel oil and had higher levels of premixed burning and lower levels of diffusion flame burning (Faletti et al. 1982). The result was higher brake thermal efficiencies, higher cylinder pressures, and increased rates of pressure rise. The energy release rates showed smooth patterns and indicated homogeneous combustion without any indication of separate combustion of the component parts.

EMA Screening Test for Endurance

The Alternate Fuels Committee of the Engine Manufacturer's Association was asked by USDA's Northern Agricultural Energy Center to develop a suitable screening test that would eliminate many of the worst candidate fuels more quickly and at less cost than with the usual tests (Alternate Fuels Committee 1982). It has been adopted by several University programs (at Alabama, Huntsville; Georgia, Athens; Idaho, Moscow; Illinois, Urbana; Kansas State, Manhattan; and North Dakota State, Fargo). Results of this test when applied to several different types of vegetable oil fuels are given in table III.

The only fuels that passed the test conclusively were the simple esters of either sunflower or soybean oil and the blend of 25 percent high-oleic safflower oil in diesel oil. The latter fuel emphasizes the negative effects imparted by polyunsaturation in the vegetable oil, i.e., when the fatty acid chain has more than one double bond.

Table III.--Engine Test Results with the EMA 200-hr Screening Procedure

Investigator	Fuel	Result
Ziejewski and Kaufman 1983a	25 Sunflower oil 75 Diesel oil	Fail (injector coking)
Kaufman and Ziejewski 1983a	Sunflower methyl ester	Pass
Kaufman and Ziejewski 1983b	Sunflower microemulsion	Fail (lube oil problem)
Ziejewski and Kaufman 1983b	25 High-oleic safflower oil 75 Diesel oil	Pass
Goering and Fry 1983	25 Soybean oil 50 No. 2 diesel oil 5 190-proof ethanol 20 1-Butanol	Pass (borderline)
Clark et al. 1983	Soybean methyl, ethyl, and butyl esters	Pass
Goodrum 1983	20 Peanut oil 80 Diesel oil	Fail (injector coking)
	80 Peanut oil 20 Diesel oil	Fail (injector coking)

The sunflower microemulsion fuel gave mixed results. On the one hand, the fuel gave a good spray pattern, and the injectors operated throughout the test in a satisfactory manner compared to the injector coking that occurred with the 25 sunflower oil/75 diesel oil blend. On the other hand, carbon and gum deposits were higher and contamination of the lubricating oil was more severe. The soybean oil/diesel oil microemulsion managed to pass the EMA 200-hr test, but there were indications that failure would have occurred had the engine been run on the fuel for a longer period.

It is apparent that more research is needed to develop more satisfactory vegetable oil microemulsion fuels. Such research can be justified on the basis that microemulsions are physical modifications of vegetable oils and that they do not introduce the processing, marketing, and quality control problems that occur with chemical modification, i.e., transesterification to make simple esters.

NEEDED RESEARCH FOR VEGETABLE OIL FUEL TECHNOLOGY

Although the simple esters of vegetable oils perform well as alternative fuels for the direct-injection diesel engine in the EMA 200-hr screening test and, apparently, have the potential of passing long-term endurance tests, considerable work is needed to obtain processing and cost information for the transesterification reaction before this fuel can be adopted generally. Other reactions, including pyrolysis, need to be examined as possible routes to more oxidatively stable, liquid fuels. Research on physical modification of vegetable oils, including microemulsion technology, needs to be continued in view of the promising results to date. It is possible that proper formulation of the microemulsions with additives may improve their performance. Such additives as dispersants and combustion improvers need to be considered.

Engine evaluations by the EMA 200-hr screening test are needed for several fuels, including:

- Methanol/vegetable oil microemulsions. Methanol is now cheaper than gasoline or diesel oil.
- Comparison between true solutions and microemulsions. Is there a detectable difference in engine results that could be attributed to the difference in these two physical states?
- Ionic microemulsions. Although ionic microemulsions are more costly than nonionic ones, they may have advantages such as greater tolerance of water.

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FUEL PROPERTIES

PRELIMINARY SPECIFICATION--VEGETABLE OIL FUEL FOR DIESEL ENGINES

T. W. Ryan, III¹

ABSTRACT

Four different types of vegetable oils, each in at least three different stages of processing, have been characterized with respect to their physical and chemical properties, their injection and atomization characteristics, and their performance and combustion characteristics in two different diesel engines.

The injection and atomization characteristics of the vegetable oils are different than those of petroleum-derived diesel fuels. Heating the oils, however, appears to make their spray characteristics more like those of diesel fuel.

Preliminary vegetable oil fuel specifications have been developed based upon the data obtained in this program. The specifications are discussed in terms of the data and the rationale that was used in their development. Complete details of the experiments are presented in a report by Ryan, et al., 1983.

INTRODUCTION

The use of vegetable oils as fuels for diesel engines is not a new concept. Since the invention of the diesel engine, the development of this engine has been based on the availability of petroleum-derived diesel fuel which, in turn, has been tailored to meet the needs of the current engines. Periodically, the vegetable-oil fuel concept has been reintroduced, usually during periods of petroleum shortages. In most cases, the interest faltered due to renewed availability of more economical petroleum-derived fuels. As a result, vegetable oils have not been developed as potential fuels nor have the desirable physical and chemical properties been defined to make them totally acceptable as a fuel source.

In summarizing the results presented in the current literature, the types of problems encountered during engine tests can be classified into two groups: operational problems and durability problems. The operational problems relate to starting ability, ignition, combustion, and performance. The durability problems relate to deposit formation, carbonization of the

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injector tip, ring sticking, and lube oil dilution or degradation. The occurrence of durability problems appears to be a very strong function of the engine type, with direct-injection engines being more susceptible than the indirect-injection engines.

Basically, three different theories can be postulated to explain the various durability problems:

1. The high viscosity of the vegetable oils results in degraded fuel atomization which, in turn, results in the observed durability problems.
2. The durability problems associated with the use of the vegetable oil fuels result directly from chemical structure of the oils and the effect of these structures on the combustion chemistry.
3. The durability problems are a result of incomplete combustion of the fuels (either spray or chemically induced) and the subsequent reaction of the fuels and/or partial combustion products on the metal surfaces and in the lube oil.

Although there is evidence that fuel chemistry affects the durability problems, the majority of evidence indicates that the high viscosity of the oils is the major factor controlling the onset and severity of the durability problems.

OBJECTIVES

The objective of this project was to develop a definition of vegetable oil fuels for diesel engines that can be used as the basis for a future vegetable oil fuel specification.

EXPERIMENTAL APPARATUS AND PROCEDURES

Fuel Characterization

The selection of vegetable oils for use as test fuels in this program represented a compromise between the range of fuel properties covered, the range of processing steps considered, and the use of oils that could realistically be considered as emergency or supplemental farm fuels in the United States. Fourteen different oils were selected. They included four soybean oils, four sunflower oils, three cottonseed oils, and three peanut oils.

All of the test oils were subjected to a variety of ASTM, AOCS, and other characterization procedures. Each oil was subjected to 28 different analyses producing approximately 50 different determinations per oil. It should be noted that the goal of physical and chemical characterization of the test oils was to document the properties of oils as well as to determine the applicability of the various ASTM fuel tests and the AOCS vegetable oil tests to the specification of vegetable oil fuels. Where necessary, the standard methods were modified in order to accommodate the peculiarities of the vegetable oils.

Spray Characterization

A device has been designed and built at Southwest Research Institute, which provides a means for examining the diesel injection event in an environment that is thermodynamically very similar to that encountered in an engine. The system consists of a bomb, a fuel injection system, and a high-speed motion picture camera.

The purpose of the bomb is to allow observation of the characteristics of diesel-type, fuel-injection sprays in a high-temperature and high-pressure environment. The design temperature and pressure are 500°C and 4.14 MPa, respectively. The temperature is maintained using electrical resistance heaters. A quiescent, inert atmosphere of nitrogen is used to prevent auto-ignition of the test fuel. The bomb has a cylindrical geometry with quartz-glass end plates that allow direct visual observation through the bomb. An injection nozzle is installed in the center section such that the spray cone is perpendicular to the axis of the cylinder.

The high-speed movies are taken using a Hycam II, 16 mm, high-speed motion picture camera. The camera is capable of running 11,000 full frames per second or, with the installation of a quarter-framing control head, at 44,000 quarter frames per second. The film speed for all of the movies was set at 25,000 quarter frames per second, or 40 μ s between frames.

Fuel injection characteristics are generally measured in terms of penetration rate, maximum penetration distance, and cone angle. Penetration rate is defined as the time rate at which the tip of the spray advances away from the injection nozzle. There is a compromise between the penetration rate and the maximum penetration distance in that a high rate of penetration is desirable, but impingement of the fuel on the surfaces of the combustion chamber is undesirable. Cone angle is defined in terms of the angle encompassed by the spray with the apex located inside the injection nozzle for real nozzles with finite diameter orifices. Cone angle is a measure of the air entrainment of the spray or, in other words, the fuel air mixing within the jet. Typically, an increase in the cone angle is accompanied by a decrease in the penetration rate.

Engine Experiments

The two test engines that were selected for use on this program are representative of those used in farming applications. The engines are turbocharged versions of the Caterpillar D-3306 design. Both engines have the same bore, stroke, and displacement, but one is a direct-injection (DI) engine while the other is an indirect-injection (IDI) engine.

The engines were coupled to eddy-current dynamometers. Engine instrumentation included a vortex-shedding flow meter on the inlet air supply, electronic weigh platforms for fuel flow measurement, and water-cooled pressure transducers for measurement of cylinder pressure. Exhaust emissions were monitored as an immediate indicator of combustion performance. Apparent heat release rates were computed from the cylinder pressure data and were used for more detailed analyses of the combustion event.

All of the vegetable oil tests were performed with the oil temperature at the injection pump maintained at 145°C, the temperature at which the viscosities of the vegetable oils are similar to that of the baseline DF-2.

EXPERIMENTAL RESULTS

Fuel Characterization

Comparison of the properties and characteristics of the various oils indicated that the oils are in many respects very similar. The only major differences appear in the contaminant levels, such as the particulate matter and the water, and in the composition of the oils with respect to the constituent fatty acids. In comparing the properties of the vegetable oils to those of the baseline DF-2, there are a number of properties where there are major differences. The flow properties, including viscosity, pour point, and cloud point, are significantly different. These differences and 6-10 percent differences in the densities could adversely affect the spray characteristics of fuel injection systems that are designed to operate with DF-2. The ignition and combustion characteristics of the vegetable oils are obviously controlled by the chemical composition of the oils, which are significantly different than DF-2.

Spray Characterization

All of the vegetable oils displayed very similar spray characteristics and very similar flow dynamics in the injection system. Comparison of the line pressure traces obtained with the baseline fuel at 40°C to the vegetable oils at 40°C revealed that the high viscosity of the oils resulted in higher overpressures than obtained with the baseline fuel. The high viscosity also resulted in dampening of the pressure oscillations in the line after injection, as indicated by a reduction in amplitude and frequency of the signal for the vegetable oil case. Comparison of the line pressure traces for the oils at the same viscosity (elevated temperature) as the baseline fuel revealed that the overpressures and oscillations were similar at these conditions.

Examination of the penetration rate data for all of the oils at a given oil temperature revealed that the degree of processing did not have a significant effect on the penetration rate of any of the oils. In addition, there were no significant differences between the four different types of oil at a given oil temperature. Oil temperature did, however, have a significant and very similar effect on all of the oils. The trends are most clearly seen in figure 1, which is the plot of penetration distance versus time for the cottonseed oils. The initial penetration rates for both temperature conditions are very similar. At approximately 150 μ s, or at 15 mm, the data for the 40°C oils indicate a slower penetration rate than the 145°C data. In other words, increasing the temperature of the oils resulted, in all cases, in an increase in the penetration rate. Accompanying the increases in penetration rate were corresponding decreases in the cone angle. In addition, the penetration rates for the oils at 40°C were lower than those of the DF-2 at 40°C, as shown in figure 1, which includes the penetration data for the baseline DF-2 as the solid line. In all cases, heating the oil resulted in increasing the penetration such that the pene-

tration plots were similar to that of the baseline DF-2. One possible explanation for this observation is the occurrence of very rapid chemical changes during the injection process.

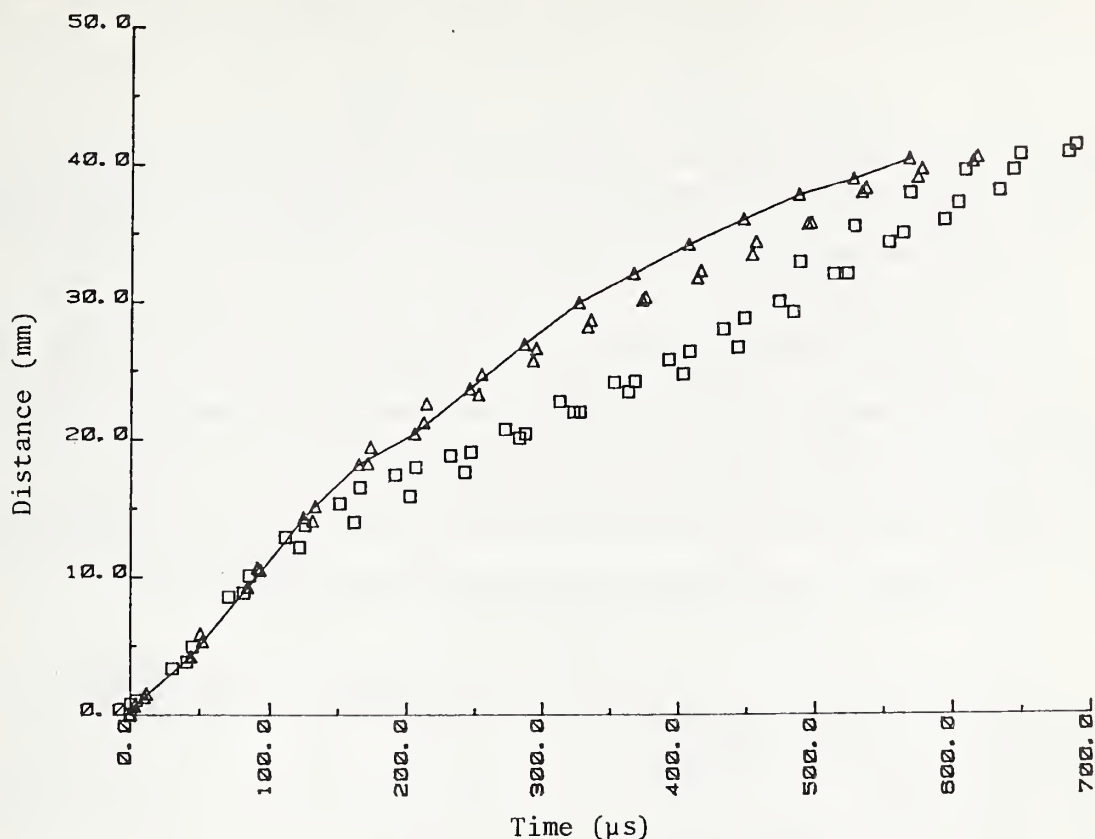


FIGURE 1.--PENETRATION DISTANCE VERSUS TIME FOR THE COTTONSEED OILS

Engine Experiments

The engine experimental data consisted of the normal measures of brake engine performance, including power, mean effective pressure, specific fuel consumption (BSFC), and specific energy consumption. Since the engine power output was always recovered (independent variable), the variables of most concern in these experiments were those related to BSFC or efficiency. The cylinder pressure, or heat release rate data, were used as diagnostics of the combustion event. Graphical comparisons and examinations of the data did not reveal outstanding differences between the vegetable oils. Statistical analyses, performed separately for each engine, revealed some significant fuel-related effects. For the DI engine, the most significant fuel properties were the ratio of linolenic/linoleic, the iodine number, and the nitrogen content. The results for the IDI engine indicated that fuel properties had less effect on the performance of this engine. The DI engine did demonstrate a fuel sensitivity for nozzle coking and lube oil dilution, which was not apparent for the IDI engine.

PRELIMINARY SPECIFICATION

Based upon the results of this study, it appears that there is a need for two different fuel specifications, one for DI engines and one for IDI engines. Table I is a listing of the recommended preliminary specifications for both engine types. It should be noted that the DI engine requirements include fairly stringent limitations on the composition of the oils. The IDI requirements, on the other hand, involve a relatively mild limit on iodine number in an effort to eliminate such potentially bad fuels as linseed oil. The specifications for both engines include a fuel temperature requirement. This was included for the IDI engines because the composition could become a factor with reduced atomization quality.

The purposes underlying the compositional limitations are to obtain maximum performance by maximizing the linolenic/linoleic ratio while still limiting the linolenic acid content to obtain the desired durability characteristics. The iodine number limits the degree of unsaturation for those oils that contain little or no linolenic acid.

Table I.--Recommended Preliminary Specifications for
Vegetable Oil Fuels for Diesel Engines

	<u>DI Engines</u>	<u>IDI Engines</u>
Cloud Point (°C), max (with heated tank)	22	22
Viscosity (cSt), max @ 140°C	5	5
Particulate Matter (mg/ℓ), max	8	8
Water (vol %), max	0.01	0.01
Copper Corrosion (rating), max	3	3
Flash Point (°C), min	38	38
Heat of Combustion (MJ/kg), min	39	39
Cetane No.	35	35
Ash (wt %)	0.01	0.01
Linolenic/Linoleic Ratio, min ¹	.07	-
Linolenic Acid (wt %), max	5	-
Iodine No., max	130	130
Thermal/Oxidative Stability	?	?

¹Applies only when the linolenic acid content is greater than 1 percent.

One important property missing from the specifications listed in table I is a measure of the thermal/oxidative stability. This property is important for the DI engine but could also have an effect in some IDI engines. A specification has not been included because of the lack of an appropriate test for diesel engine fuels.

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EFFECTS OF STRUCTURE OF FATTY ACID ESTERS

ON EFFICIENCIES AS DIESEL FUELS

W. E. Klopfenstein and H. S. Walker^{1/}

Vegetable oils generally contain the same fatty acids but may differ greatly from one another in the proportions of the individual acids present. In an attempt to determine whether any particular fatty acid might possess especially good or bad qualities as a diesel fuel, we have been studying the properties of purified esters of fatty acids as diesel fuels. We have studied the effects of structure of the fatty acid (chainlength and unsaturation) and the structure of the alcohol used to make the ester.

Commercial fatty acids were used to make most of the esters. Most of the acids were obtained from Eastman although the decanoic and lauric acids were provided by Armak Chemical Co., McCook, Ill. The esters were prepared using H_2SO_4 as catalyst. The esters were recovered, washed with H_2O , dried with anhydrous Na_2SO_4 , and purified by vacuum distillation. The fatty acid composition was determined by gas liquid chromatography. Densities and heat contents of the esters were determined.

Engine tests were carried out on a 3.9 KW Fairbanks-Morse diesel engine driving an electric dynamometer. During the tests, the engine was run at rated load and speed. Times required to burn 100 ml of fuel were measured. These data were converted to specific fuel consumptions. Specific fuel consumptions were converted into efficiencies, using the heat contents of the individual fuels and the heat equivalent of the work done by the engine.

Efficiencies of the methyl esters of the saturated fatty acids as related to chain length are shown in figure 1. This shows that efficiency is generally inversely related to chain length of the fatty acid, except that for the very short chain esters the efficiency is again lower. Efficiency appears to peak at methyl decanoate. Whether the acid is saturated or unsaturated also affects efficiency. We have previously shown (1) that the esters of the eighteen carbon unsaturated acids burn with higher efficiency than does methyl stearate.

The alcohol esterified also appears to slightly affect the efficiency of the esters as diesel fuel. Table 1 lists the efficiencies of decanoic acid and several decanoic esters as fuels. The esters, other than that of 1-propanol, all show higher efficiency than the free acid, with the butyl

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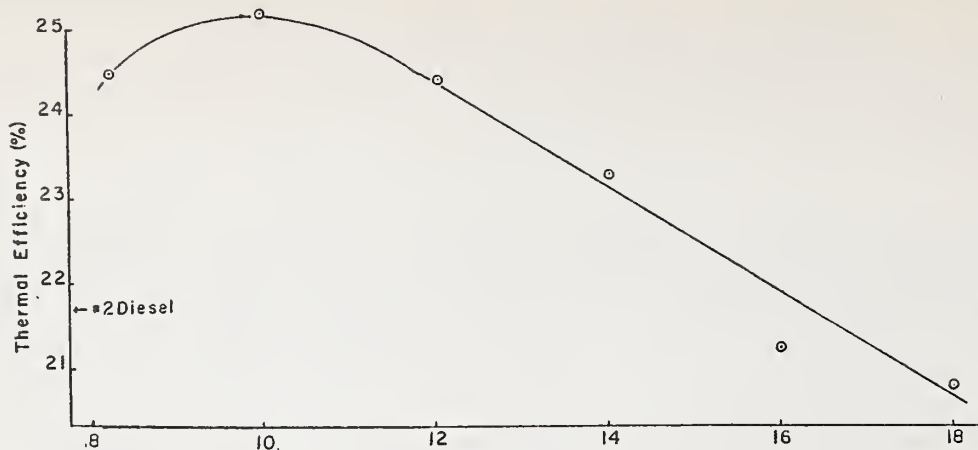


Figure 1.--Fatty acid chain length.

ester having the highest efficiency of the series. A similarly increased efficiency for the butyl ester relative to the methyl ester was observed with octanoic acid. The elevated efficiency for the butyl ester is in contrast with our earlier results (1) with esters of oleic acid. In that study we found that the efficiency of butyl oleate was lower than that for the methyl or ethyl esters.

Table 1.--Efficiencies of derivations of decanoic acid as fuels in a diesel engine

Fuel	Efficiency (pct)
H ⁺ 10:0	24.8
Me 10:0	25.1
Et 10:0	25.1
1-Pr 10:0	24.8
2-Pr 10:0	25.1
Bu 10:0	25.8

This study has found that structure of the fatty acid portion of the ester greatly influences the efficiency of the ester as a fuel. Efficiency peaks at the decanoic ester for the methyl ester series and decreases with either shorter or longer chain length. Unsaturation increases efficiency relative to the corresponding saturated ester. The alcohol esterified in the ester seems to have a lesser effect on efficiency than either fatty acid chain length or unsaturation.

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RELATIONSHIP BETWEEN CETANE NUMBER AND STRUCTURE FOR

FATTY ACID ESTERS

W. E. Klopfenstein^{1/}

There has been much interest lately in the use of vegetable oils and esters derived from vegetable oils as alternative fuels for diesel engines. This has included tests on fuels derived from a large variety of oils and talk of breeding crops specifically for fuel use. Since the various oils differ from one another primarily in their fatty acid compositions, I have been studying the esters of the individual fatty acids as fuels.

Cetane numbers for triglycerides are difficult to determine by standard techniques although they may be readily determined for esters prepared from the oils, and cetane numbers for several such mixtures have been reported (1). I now report the cetane numbers of several relatively pure fatty acid esters. These esters differ in the chain length and degree of unsaturation of the fatty acid and the structure of the alcohol esterified.

Most of the esters were prepared from commercial grades of fatty acids obtained from Eastman although the decanoic and lauric acids were provided by Armak Chemical Co., McCook, Ill. One preparation of methyl linoleate was made by transesterification of safflower oil while methyl linolenate was prepared from linseed oil. The esters were vacuum distilled and analyzed by GLC for purity. Purities ranged from approximately 57 percent for methyl linolenate to 100 percent for the esters of the shorter chain saturated acids. Cetane numbers were determined by Waukesha Engine Division, Dresser Industries, Waukesha, Wis. Cetane numbers have not been corrected for the purity of the esters.

Table I shows that for the methyl esters of the saturated acids the cetane number increases with chain length of the acid. Preliminary evaluation of these data suggests that the increase in cetane number is not linear with chain length of the acid. Unsaturation of the fatty acid leads to a lower cetane number for the ester. Methyl linoleate has a lower cetane number than methyl oleate, suggesting that the greater the degree of unsaturation the lower will be the cetane number. Methyl linolenate appears to violate this rule. However, the preparation of the methyl linolenate took place over a long period of time, providing an opportunity for auto-oxidation, and the sample had a peroxide value of 14. Azev et al. (2) found that the formation of hydroperoxides in diesel fuel raised the cetane number. Thus the presence of the peroxides in the methyl linolenate might explain the higher than expected cetane number.

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The type of alcohol esterified also affects the cetane numbers. Table I contains cetane numbers for esters other than methyl for three acids. In all cases, the ethyl esters show increased cetane numbers. The general trend is that, with a given acid, esterification of a higher molecular weight alcohol results in an elevated cetane number. There is one exception to this pattern. The isopropyl ester of decanoic acid has the lowest cetane number for the series.

The results to date suggest the following generalities:

1. Cetane number increases with molecular weight of the fatty acid.
2. Cetane number increases with molecular weight of the normal series of alcohols.
3. Cetane number decreases with unsaturation of the fatty acid.

The contributions of molecular weight in 1 and 2 may not be the same.

Table 1.--Cetane numbers of fatty acid esters

Ester	Common Name	Purity (pct)	Cetane #
Me 8:0	Methyl Octanoate	98.6	33.6
Bu 8:0	Butyl Octanoate	98.7	39.6
Me 10:0	Methyl Decanoate	98.1	47.2
Et 10:0	Ethyl Decanoate	99.4	51.2
i-Pr 10:0	Isopropyl Decanoate	97.7	46.6
n-Pr 10:0	Propyl Decanoate	98.0	52.9
Bu 10:0	Butyl Decanoate	98.6	54.6
Me 12:0	Methyl Laurate	99.1	61.4
Me 14:0	Methyl Myristate	96.5	66.2
Et 14:0	Ethyl Myristate	99.3	66.9
Bu 14:0	Butyl Myristate	99.0	69.4
Me 16:0	Methyl Palmitate	93.6	74.5
Me 18:0	Methyl Stearate	92.1	86.9
Me 18:1	Methyl Oleate	90.7	52.5
Me 18:2	Methyl Linoleate	79.0	42.6
Me 18:3	Methyl Linolenate	56.6	46.6 ¹

¹Peroxide value of 14

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EMA SCREENING TESTS

ALTERNATIVE FUELS FOR DIRECT INJECTION DIESEL ENGINES

M. Z. Ziejewski, K. R. Kaufman, and G. L. Pratt^{1/}

ABSTRACT

Laboratory endurance tests were performed on a direct injected, turbocharged, and intercooled diesel engine. A 25/75 blend (v/v) of alkali refined sunflower oil with diesel fuel, a 25/75 blend with Lubrizol additives, nonionic sunflower oil-aqueous ethanol microemulsion, methylester, and a 25/75 (v/v) of high oleic safflower oil and diesel fuel were tested. For comparison prior to the tests with the experimental fuels, a baseline endurance run with Phillips D2 Reference Fuel was carried out.

Based on the results of this investigation, the 25-75 blend of high oleic safflower oil with diesel fuel and the methylester is a very promising candidate as an alternate fuel.

INTRODUCTION

Because vegetable oils have much greater viscosities and are much less volatile than diesel fuel, problems have arisen when vegetable oils have been used as an alternate fuel for diesel engines. Viscosity for tested fuels was reduced by (a) diluting the vegetable oil with diesel fuel, thereby forming blends that have been termed hybrid fuels, (b) converting the vegetable oil to the simple esters of methyl alcohol, and (c) by microemulsification.

The test on the 25/75 blend of high oleic safflower oil and diesel fuel was conducted to answer the question of the relative importance of vegetable oil saturation/unsaturation. The alkali-refined sunflower oil and the high oleic safflower oil were chosen because they represented a range of vegetable oil iodine values grown in the United States.

The purpose of this project was to study the effect of different alternative fuels on the performance and durability of a direct injected, turbocharged, and intercooled diesel engine.

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EXPERIMENTAL PROCEDURES

Materials

The fuels utilized in this project were D-2 diesel control fuel (Phillips Reference Fuel), the 25-75 blend (v/v) of alkali refined sunflower oil-diesel fuel, the 25-75 blend with Lubrizol additives (barium smoke suppressant Lubrizol 565 and detergent-dispersant additive Lubrizol 552), nonionic sunflower oil-aqueous ethanol microemulsion, methylester, and 25-75 blend (v/v) of high oleic safflower oil - diesel fuel. All fuels were obtained from commercial services. Samples of the test fuels were analyzed, using American Society of Testing and Materials (ASTM) standard procedures. Results presented in table 1 show several important properties of the fuels that influenced engine performance and durability.

Table 1: Test Fuel Properties

	D-2 Control Diesel Fuel	25-75 Sunflower Oil Blend	25-75 High Oleic Safflower Oil Blend	Methylester	Nonionic Microemulsion
Pour Point, °C	-29	-32	-29	-4	Note 2
Cloud Point, °C	-20	-20	-22	0	15
API Gravity @ 15.6°C	35.5	31.6	31.9	27.8	31.3
Heat of Combustion, KJ/kg					
Cross	45,422	43,719	43,761	39,796	36,393
Net	42,668	41,082	41,073	37,202	33,592
Heat of Combustion, KJ/L					
Cross	38,399	37,845	37,813	35,272	31,559
Net	36,071	35,561	35,490	32,974	29,130
Viscosity @ 40°C, cs.	2.37	4.88	4.92	4.22	6.31
Viscosity @ 100°C, cs.	--	1.55	1.81	1.97	2.16
Cetane Number	50.1	45.4	47.5	46.6	< 5
Ash, %	< 0.01	< 0.01	< 0.01	0.0014	< 0.01
Carbon, %	86.92	84.03	84.37	76.72	70.78
Hydrogen, %	12.46	12.43	12.67	12.22	13.20
Sulfur, %	0.23	0.12	0.13	< 0.005	0.01
Flash Point, FMCC, °C	--	82.8	82.8	Note 1	27
Peroxide Value, meq/1000 g.	--	12.96	2.32	22.8	15.99
Total Acid No., mg KOH/g.	--	0.03	0.01	0.14	0.02
Free Fatty Acids, %	--	< 0.01	< 0.01	0.07	0.01
Iodine Value	--	52.35	42.19	133	72.6

Note 1: Above 85°C sample vapors burn outside of cup and extinguish test flame. No flash observed up to 177°C

Note 2: The sample exhibits a cloud point at 26°C. At 2°C the sample separated into two phases. The lower (white) layer solidified at -29°C, the upper (pink to yellow) layer was still liquid at -65.0°C.

The high oleic safflower oil represented an oil that had a fair degree of saturation (iodine value = 92) and yet was a liquid at normal ambient conditions (pour point = 29°C). In contrast, the sunflower oil was polyunsaturated (iodine Value = 133). The analysis showed the composition of the alkali refined sunflower was 6.0 percent palmitic, 4.2 percent stearic, 18.7 percent oleic, 69.3 percent linoleic, 0.3 percent linolenic, 0.4 percent arachidic, 0.1 percent eicosenoic, and 1.0 percent behenic. High oleic safflower oil was 5.2 percent palmitic, 2.2 percent stearic, 76.3 percent oleic, and 16.2 percent linoleic.

The microemulsion composition was 53.3 percent (volume) sunflower oil, 13.3 percent (volume) 190-proof ethanol, and 33.4 percent (volume) 1 butanol and remains a homogeneous single phase system down to 15°C.

Test Procedure

A four-cylinder Allis-Chalmers model 433 I turbocharged and intercooled four-stroke cycle diesel engine was used for fuel evaluation. The displacement of the engine was 3.28 L (98.43-mm bore, 107.95-mm stroke), the compression ratio was 14.5:1. A Stanadyne Roosa Master Distribution Pump Type DB2 was used with two 9.40-mm pumping plungers. The injection nozzle used was a Robert Bosch nozzle with four 0.32-mm diameter orifices, a 1.1-mm sac length, and a 1.0-mm sac diameter. The engine was operated on a screening-test cycle recommended by the Alternate Fuels Committee of the Engine Manufacturer's Association (EMA) (AFC, EMA 1982). The cycle was repeated five times. After 15 hours on the cycle, the engine was shut down for nine hours. This procedure was repeated until 200 hours of operation on the test cycle had been completed. Average cycle power was maintained at about 70 percent. Engine load was applied with a Dynamic Absorbing Dynamometer Model 1014 D.G. A Hytress III Simulator System was used to simulate the programmed-engine cycle, which was recorded on magnetic tape in frequency modulated (FM) form. Fuel injection line pressure was measured at the nozzle with a Kistler Model No. 607F122 piezoelectric pressure transducer. Fuel consumption was measured on a weight basis with a Cox Instrument Fuel Consumption Weight System, Type 402. A Robert Bosch (RB) Model EFAW 68A smokemeter was used to analyze exhaust smoke.

RESULTS AND DISCUSSION

Engine Performance

The differences in the initial engine performance between the reference fuel and tested fuels were generally caused by differences in energy delivery. The higher viscosity of the tested fuels contributed to an increase in volumetric fuel flow by reducing internal pump leakage. However, the higher volumetric fuel flow for tested fuels was not sufficient to compensate the lower heating value compared to the diesel fuel. Significant differences between the tested fuels were observed in the exhaust smoke emission. For the 25-75 sunflower oil blend, the initial RB smoke was higher compared to the diesel fuel. The other fuels showed lower RB smoke, particularly the microemulsion and 25-75 sunflower oil with Lubrizol additives produced very low exhaust smoke level. The barium suppressant additive Lubrizol 565 markedly increases power output, decreases break specific fuel consumption (BSFC) and smoke compared with the reference diesel fuel. However, this Lubrizol additive leads to the formation of barium particles at a greater concentration compared to the carbon particle concentration produced by the untreated diesel fuel or 25-75 blend. Excessive deposits after a short period of time caused a sharp loss in engine power; rise in the exhaust smoke level accompanied simultaneously by increase in BSFC was experienced. Deterioration of the engine performance does not appear to be influenced by additive concentrations in the tested range of 0.125 percent to 0.5 percent. In comparison, the 25-75 blend with 0.03 percent of Lubrizol 552 showed stable performance. The engine

performance on the 25-75 safflower oil blend, microemulsion, and methyl-ester throughout the entire test was adequate. During the 25-75 sunflower oil blend test, in order to maintain the required power output (rated power \pm 5 percent), a set of injection nozzles was changed after 76 hours of engine operation.

Injection System

In this investigation, particular attention was devoted to the injection system performance. Based on previous experiments, a new fuel injection pump and a new set of injection nozzles were used prior to each test. After the test on diesel fuel, all tips showed normal carbon residue. Inspection indicated only a slight reduction in orifice diameters due to carbon buildup. The highest nozzle opening pressure drop was 10 percent. For all tested nozzles after the 25-75 sunflower oil blend test, normal carbon residue on the nozzle tips and abnormal reduction in orifice diameters due to carbon buildup were observed. Nozzle #1 had one plugged orifice. The nozzle opening pressure drop was 7 percent and was uniform for all nozzles. The lacquer buildup on the injection nozzle needle over a period of time caused the needle movement in the housing to become difficult or impossible. The sporadic nozzle needle sticking did not directly effect the BSFC, but it contributed to the formation of carbon deposits on the nozzle tip, nozzle needle, and nozzle seat.

Contrary to the 25-75 sunflower oil blend test, an injection nozzle stand test indicated proper nozzle functioning after 254 hours of operation on the high-oleic safflower oil mixture. Inspection showed uniform carbon buildup on all nozzle tips and only a slight reduction in orifice diameters for all nozzles.

Inspection of the injection nozzle parts after the 25-75 blend with additive Lubrizol 565 showed improved nozzle cleanliness. However, on the injection nozzle tips, excessive, irregular deposits around the orifices were formed. From the exhaust valve side, carbon residue reached a height of approximately 1.5 mm. Deposits did not appear to be blocking any orifice. The Lubrizol 552 (0.03-percent v/v) as an additive to the 25-75 sunflower oil blend also improved nozzle cleanliness but did not cause formation at the abnormal carbon buildup. During the test on the microemulsion, the injection nozzle needles stuck sporadically for various nozzles. The final nozzle-opening pressure drop was 6.5 percent for two nozzles and 5 percent for the remaining two nozzles. The injection nozzle tips displayed slightly heavier carbonaceous residue, which did not appear to block any orifices. After the test on the methylester, the fuel stand nozzle analysis indicated proper nozzle function. The drop in final nozzle-opening pressure was small and uniform. Inspection showed uniform, slight reduction in orifice diameter due to carbon build-up.

The fuel injection pumps performed properly throughout all tests. However, after the run on the microemulsion, excessive deposits on the internal parts of the pump and an increase in the flexibility of a flexible ring in the weight cage were recognized.

Lubricating oil

The lubricating oil consumption, viscosity, and lube oil dispersivity characteristic for diesel fuel, 25-75 sunflower blend, and 25-75 safflower blend test were adequate.

For the methylester run, some fuel dilution of the lube oil indicated by an initial reduction in the lubricant viscosity and later lubricant thickening was observed. Throughout the run on the microemulsion, the lube oil consumption varied. Several times the lube oil level increased, indicating significant fuel dilution of the lube oil. Oil samples, taken every 15 hours, were used to determine any changes in kinematic viscosity and dispersivity characteristics. After 60 hours of the EMA cycle (80 hours since the last lube oil was changed), a 50-percent change of kinematic viscosity was noted. After 120 hours of the EMA cycle (78 hours since the lube oil was changed), a sudden increase in lube oil viscosity from 108 cPs to 2280 cPs was observed. Except for the samples of the lube oil for the microemulsion test at 60 and 120 hours of the EMA cycle, analysis of the "blotter spot" samples did not indicate abnormal changes in the lubricant dispersivity characteristics.

Engine Teardown and Final Inspection

After each durability test, the carbon, sludge, and varnish deposits were rated, using the Coordinating Research Council test procedure (CRC 1959).

Heavier carbonaceous accumulation underneath the valve seat and in the combustion side of the intake ports for the 25-75 sunflower oil blend and microemulsion did not appear to significantly influence the air flow. During the microemulsion test, the difficulty in exhaust valve movement due to carbon buildup on the valve stems caused pistons #1, #2, and #4 to hit the exhaust valves. Subsequently, exhaust valve stem deformation occurred. For the same fuel, heavier and hard carbon residue was observed on the cylinder sleeves above the ring travel area. For all tested fuels, the cylinder sleeves had only random skirt scratching and light polish tracks. The pistons for all tested fuels did not exhibit any sign of cracking but, in the case of 25-75 sunflower oil blend and microemulsion, greater carbon and lacquer buildup in the ring grooves and on the piston lands was observed. For the 25-75 sunflower oil blend on all pistons, the second rings were sluggish. After the microemulsion test, the second ring for pistons #3 and #4 and the third ring for piston #2 were partially stuck on 180° of circumference on the antithrust side.

The average CRC rating for the top piston land deposits was the highest for the microemulsion (1.92), then for the 25-75 sunflower oil blend (1.68) methylester (1.65), 25-75 sunflower oil blend with additives (1.42), diesel fuel (1.47), and the lowest rating was for the 25-75 safflower oil blend (1.33), where the higher number corresponds to a poorer rating. A similar trend can be observed by analyzing the second piston land, the piston groove carbon filling, and piston ring carbon deposits. All deposits from the tests on the experimental fuels appeared to be hard and shiny and did not flake off compared with the dry carbon buildup formed during the run on diesel fuel.

Rod and main bearings after all tests were in good condition. No deposits were visible. All bearings showed a normal wear pattern. Turbochargers were in satisfactory condition; the turbine wheels were covered with normal light carbon residue. Compared with initial measurements, the final results for engine measurements did not indicate significant wear.

CONCLUSIONS

1. The results of this investigation showed that the major problems involving the use of vegetable oil as a diesel fuel substitute are:
 - (a) Premature nozzle deterioration (sporadic injection nozzle needle sticking and carbon build-up in the nozzle tip orifices).
 - (b) Carbon deposits in the ring grooves and on the piston lands.
 - (c) Fuel dilution and increase in the viscosity of the lube oil.
2. Based on the results of this investigation, the 25-75 sunflower oil blend cannot be recommended for long-term use in direct injection engines without further research work.
3. Compared to the engine run on diesel fuel and untreated 25-75 mixture, the barium smoke suppressant additive Lubrizol 565 proved to be effective in cleaning the inside of injection nozzles (no needle sticking, no carbon build-up inside the orifices) and reducing diesel exhaust smoke. However, there was increased deposit accumulation in the combustion chamber and on the injection nozzle tips. The detergent-dispersant additive Lubrizol 552 looks very promising. Normal carbon buildup on the nozzle tips, top of the pistons and cylinder head, and stable performance was observed.
4. Further investigations and tests are necessary before sunflower oil/aqueous ethanol/1-butanol microemulsions can be considered as alternate fuels for diesel engines.
5. Based on the results of this investigation, it is evident that the chemical differences between the vegetable oils (saturation level) have an important influence on long-term engine performance.
6. The 25-75 high oleic safflower oil blend and the methylester successfully completed 200 hours of the EMA cycle. Nevertheless, at this point, a final recommendation still cannot be made until a field durability test is performed to establish the long-term effect of the fuel on engine performance.

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PEANUT OIL AS AN EMERGENCY FARM DIESEL FUEL

J. W. Goodrum^{1/}

ABSTRACT

Long-term engine tests of 20:80 and 80:20 crude peanut oil:#2 diesel blends have been conducted on the E.M.A. test cycle. Simultaneous tests of two indirect injection high speed engines provide minimal statistical base for results. Comparative direct injection tests are currently underway.

Tests to date indicate a 5 percent power loss after 130 hours of E.M.A. cycle on 20:80 peanut:diesel. For 80:20 peanut:diesel, a 5 percent power loss is observed after about 50 hours. Full power is restored by cleaning injectors. Ring sticking or other abnormal wear has not been observed. High soot levels in crankcase oil, elevated exhaust temperatures, for coked injectors, and varying specific fuel rates were documented.

INTRODUCTION

In order to prepare for possible future shortages of agricultural diesel fuel, we are examining the technical aspects of a farm fuel system based upon peanut oil. Emphasis is placed on equipment and methods that could be used in the near term. In general, simple procedures and low-cost farm or community-scale equipment have been emphasized. The fuel produced should be a direct substitute for #2 diesel fuel, requiring a minimum of changes to engine or engine-operating procedure.

In order to evaluate the potential of an emergency fuel system based on peanut oil, we are reviewing growth/harvest methods, storage of peanuts or oil, simple oil extraction technology, fuel blend properties, and engine durability. In each case, preliminary technical feasibility is being examined.

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Vegetable oils, such as peanut oil, offer one of the most direct and least capital-intensive routes to a non-petroleum diesel fuel for agriculture. The technology for oil production is relatively simple and efficient. In the case of peanuts, filtered crude-pressed oil can be used directly in diesel engines. The current production of peanuts and other oilseeds could provide a significant fraction of the on-farm diesel need, so the raw material for this alternative fuel is already available.

Previous study in this area includes a review by Quick (1) of the potential of a number of vegetable oils, including peanut oil, as alternate diesel fuels. Goodrum and Law (2) have measured rheological properties of peanut oil/diesel blends. Extensive engine reliability tests of sunflower and canola oils have recently been conducted (3,4).

OBJECTIVE

The objectives of the work described in this report are to identify long-term effects on diesel engines that are operated on peanut oil/diesel blends. In this report, we describe tests of indirect injection engines.

EQUIPMENT AND PROCEDURE

The two Kubota model D850 test units are 3-cylinder water-cooled engines having 22:1 CR, 0.85ℓ displacement, and 15 kW output (20 H.P.) at 3,000 rpm. These engines are believed to be good examples of current high-speed indirect injection design. Twenty kW alternators (Winco model KS, 3600 rpm) were coupled 1:1 to the engines by notched belt drive (see fig. 1). This drive system permitted a simple, low-cost power measurement method. A strain gage bridge on the engine crankshaft is monitored via slip ring unit (Michigan Scientific Model 8U). Engine loading was accomplished by external adjustment of alternator field current. The above arrangement would have permitted fully automatic control of engine output; however, manual control was simple and effective. Electrical output (kW) was used as a guide for maintaining constant engine output. Alternator power was dissipated in resistance type air heating elements (220 V).

Sensors for fuel flow, temperatures (cooling water, exhaust, and fuel), rpm, and torque were installed on both engines and interfaced with the data system.

The data acquisition system for real-time data processing included the components described below. Key components are the twelve-channel A/D converter (Analog Devices μ -Mac 4000) and an Apple microcomputer (64K memory and mountain computer clockboard accessory). An electronic counter was fabricated and installed in the Apple for processing fuel flow data. Software functions programmed in the Apple included baseline corrections, units conversion, time markers for data, and magnetic data storage.

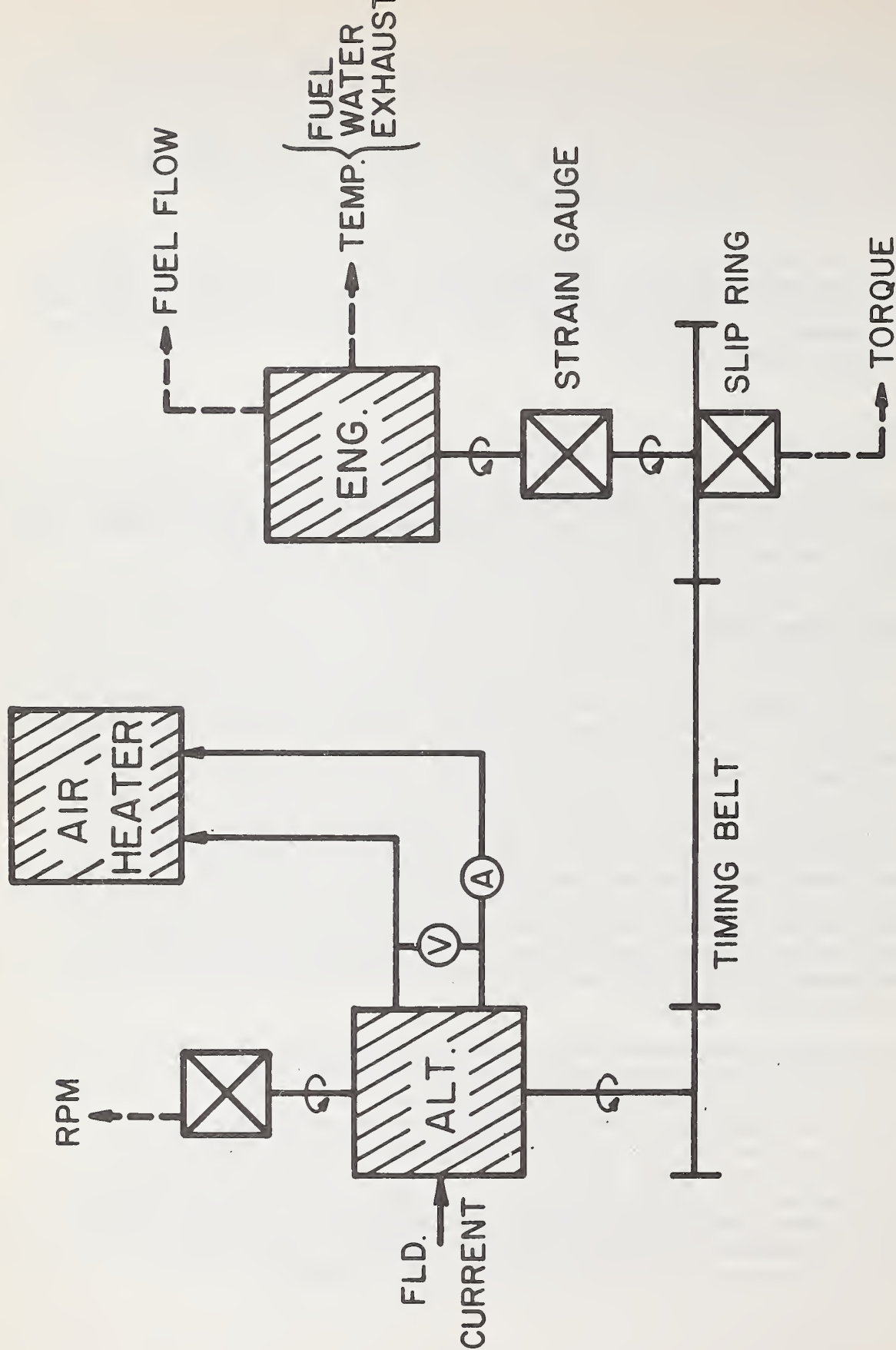


Figure 1. Schematic of Sensing and Loading Devices on Engine.
(Reprinted from ASAE #83-3026)

Data are collected at one-minute intervals, displayed as bar graphs on the monitor, printed on a chart as percent of maximum value, and recorded on a magnetic disk. Real-time processing permits constant observation of sensor outputs so that malfunctions of equipment are quickly seen and repaired.

Fuel blends were prepared from crude peanut oil (supplied by Gold Kist Co., Atlanta, Ga.) and #2 diesel. A 30-minute period of recirculation by pump (10 gpm) provided uniform mixing for 190ℓ (50 gal) blend volumes. After blending, fuel is pre-filtered to approximately 0.4 micron, using bus diesel fuel filters.

The E.M.A. (Engine Mfg's Assn.) Alternate Fuels Test Cycle was followed for up to 200 hours. This procedure is designed to detect power output, fuel efficiency, unusual wear, and crankcase oil degradation during long-term tests. Phillips #2 Reference Fuel provided baseline values of output and efficiency before and after tests with peanut oil blends. The crankcase oil was evaluated at 15-hour intervals. A commercial analysis service (Optimal Systems, Inc., Atlanta, Ga.) found wear metals, oil viscosity, moisture, and solids.

Tests with two engines were conducted for 200 hours on the E.M.A. cycle, using 20:80 peanut oil/diesel blend. Using two engines improves the statistical base. When maximum power output dropped 5 percent, the fuel filters, air cleaners, injectors, etc., were examined and cleaned as necessary so that output power was restored. Testing then continued on the E.M.A. cycle. At 200 hours, the combustion chamber, piston rings, and valves were examined.

The two engines were next operated with an 80:20 peanut oil/diesel blend, using the E.M.A. procedure. Injectors, etc., were changed when a 5-percent loss was observed. This test continued for 120 hours.

Analogous tests with two direct injection engines are now underway. These are single cylinder 16:1 CR water-cooled units developing 5 kW at 2400 rpm.

RESULTS

Results of Engine Durability Tests, 20 Percent Peanut Oil/Diesel Blend

After 130 hours on the E.M.A. cycle, a 5-percent decrease in maximum power was observed. At this point there was also a measurable increase in exhaust temperature and specific fuel rate (see fig. 2). After scraping coke from the injectors, full power was restored. At 200 hours, the engine rings were free, and very moderate carbon deposits were present in the combustion chamber, primarily near the injector. The crankcase oil contained abnormally high soot deposits after about 30 hours' operation. However, wear metals were normal after the break-in period.

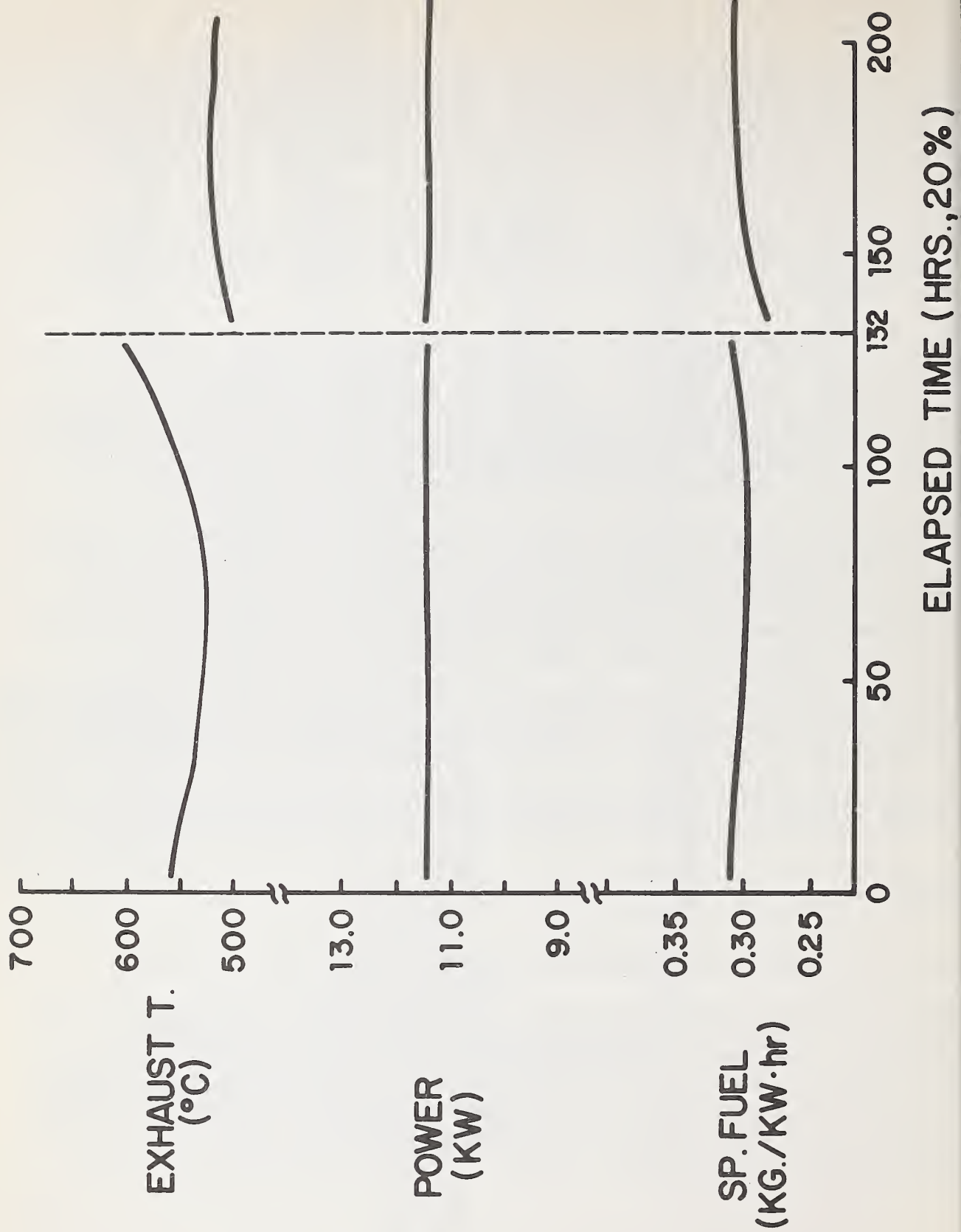


Figure 2. Schematic of Data Acquisition and Loading System for Engines.

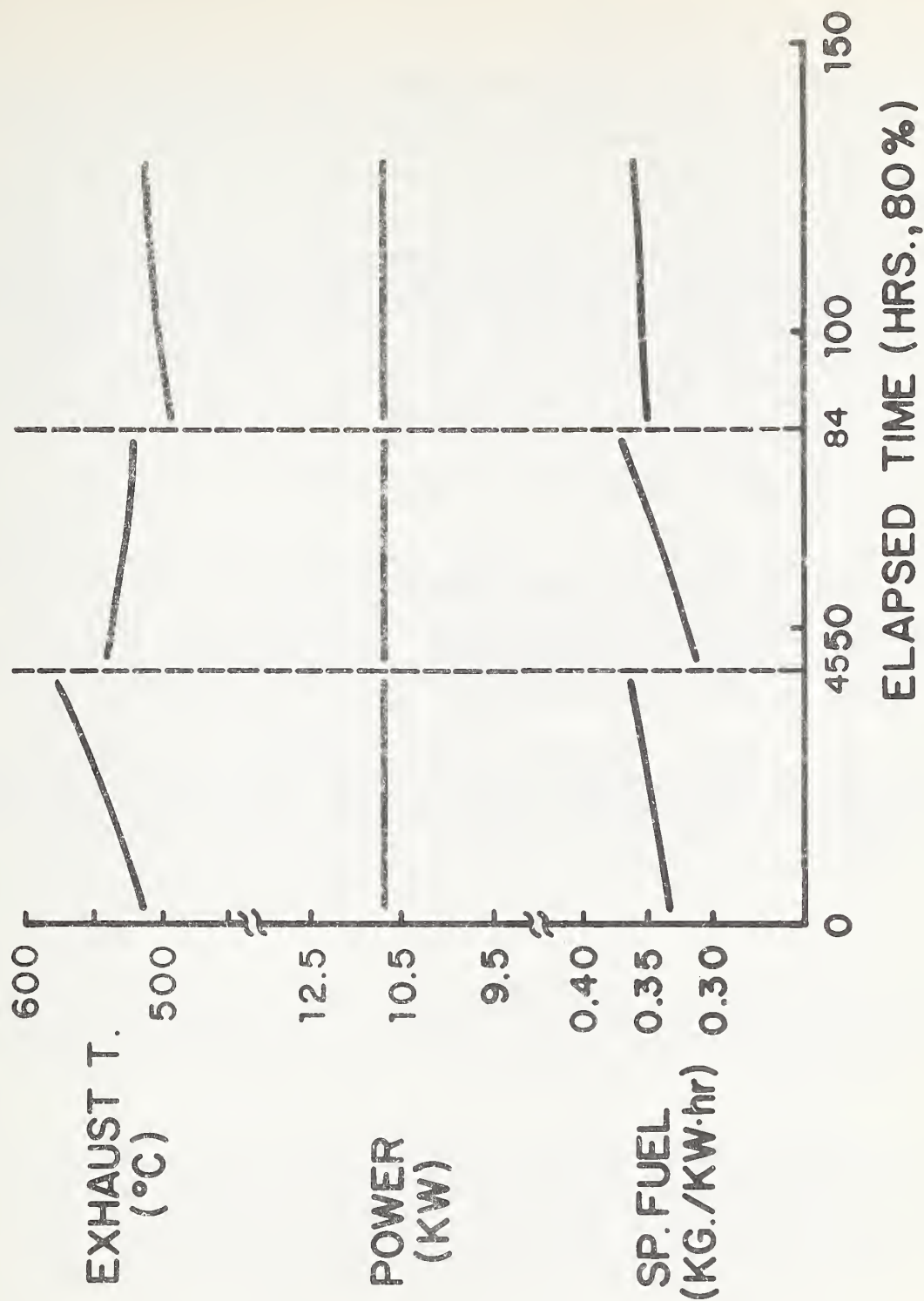


Figure 3. Average Performance of Two Engines Operated on 80:20 Peanut Oil/Diesel.

80 Percent Peanut Oil/Diesel Blend

After 45 hours on the E.M.A. cycle, the maximum power had decreased 5 percent. As with the 20 percent blend, exhaust temperature and specific fuel had increased as injector coking developed (see fig. 3). The cleaned injectors then operated for 40 hours more before a 5-percent power decrease was detected. The engines were disassembled at 130 hours. All rings were free, and compression pressure was within new engine specifications. There was a thin, hard deposit on carbon in the combustion chamber. The intake valves had a thin, irregular deposit on the stem. The crankcase oil contained soot at about the same level as for 20-percent blends. Wear metals in oil were normal for diesel engines.

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METHYL, ETHYL, AND BUTYL SOYBEAN ESTERS AS A RENEWABLE FUEL FOR DIESEL ENGINES

S. J. Clark, L. Wagner, M. D. Schrock, and P. G. Piennaar¹

ABSTRACT

Two-hundred hour fuel-screening tests were performed on a John Deere 4239 TF direct injected, turbocharged diesel engine using ethyl, methyl, and butyl esters of soybean oil as a fuel. An additional 200-hour test was performed using Phillips reference diesel fuel to provide a standard of comparison. Engine performance tests showed that the ester fuels compared very well with the diesel reference fuel. Emissions tests showed that nitrous oxide levels were higher for the ester fuels. Engine blueprinting and oil tests indicated that wear rates of the ester fuels were comparable with the diesel reference fuel.

INTRODUCTION

Recently, renewed interest in vegetable oils led to the testing of sunflower oil esters by Bruwer (1980) as a fuel for diesel engines. The ester form of sunflower oil has fuel properties that compare far better with diesel fuel than does pure sunflower oil. Dynamometer tests revealed that after 100 hours of operation at 80 percent of maximum power, the ester fuels actually caused less injector-tip fouling than diesel fuel and yielded higher brake thermal efficiencies and lower smoke values.

The objectives of this investigation were a) to determine how the physical properties of soybean oil, ethyl, methyl, and butyl esters compare with a standard diesel fuel and b) to perform medium term tests on a direct injection, turbocharged diesel engine to determine how wear, oil deterioration, exhaust emissions, and performance for a soybean oil, ester-fueled engine compared with a #2 diesel-fueled engine.

FUEL PROPERTIES

Transesterification is the process of reacting a triglyceride with an alcohol in the presence of a catalyst to produce glycerol and fatty acid esters. The molecular weight of a "typical" ester molecule is roughly one-third of that of a "typical" soybean oil molecule and has a much lower viscosity.

Since the viscosity of the fuel was of prime concern because of its effect on injector nozzle spray patterns, extensive viscosity tests were done to determine how much the transesterification process did change the viscosity. Using a temperature-controlled water bath and Ubbelohde type viscometers, viscosity tests were performed, in compliance with ASTM D445, on #2 diesel fuel, and the ethyl, methyl, and butyl soybean oil esters. From table

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2, it can be seen that a significant reduction in viscosity occurred and that the viscosities of the esters are close to diesel fuel.

The test fuels, #2 reference fuel and the soybean esters (trade name ethyl soyate, methyl soyate, and butyl soyate), were purchased from Phillips Petroleum and Emery Industries, respectively. Table 1 shows the fatty acid composition of degummed soybean oil and the ethyl, methyl, and butyl esters of soybean oil.

TABLE 1.--Fatty Acid Composition (percent by wt.) of Soybean Oil and Esters

Fatty Acid	Formula	Degummed			
		Oil *	Methyl	Ethyl	Butyl
Myristic	C14	0.1	0.05	0.4	0.0
Palmitic	C16	10.76	9.6	10.1	12.2
Margariz	C17	0.17	0.0	0.0	0.0
Stearic	C18	4.13	4.5	5.7	4.6
Iso-Stearic	ISO-C18	0.1	0.0	0.6	0.0
Arachidic	C20	0.33	0.3	0.0	0.3
Behenic	C22	0.07	0.0	0.2	0.0
Palmitoleic	C16:1	0.23	0.1	0.8	0.1
Oleic	C18:1	23.03	22.35	22.2	22.9
Gadoleic	C20:1	0.07	0.0	0.2	0.0
Linoleic	C18:2	52.67	54.35	51.2	52.7
Linolenic	C18:3	7.6	8.35	6.5	7.1

* The average value is given for all three lots of crude degummed soybean oil that were used to make the esters.

These values are typical for soybean oil but are known to be influenced by many conditions such as climate, variety, soil type, etc. Other properties related to the esters are shown in table 2.

An additive package was added to the ester fuels in order to improve some of the fuel properties. The additives were supplied by Ethyl Corporation and consisted of Ethyl Distillate Additive-2, Distillate Ignition Improver-3, and Cold Flow Improver-42. The EDA-2 contains an antioxidant, a detergent dispersant, metal deactivator, corrosion inhibitor, and an emulsification agent. The DII-3 provides a gain in diesel cetane number of about 5. The CFI-42 acts as a pour-point depressant. The following treatment rates were used: EDA-2: 0.02 percent by weight; DII-3: 0.1 percent by volume; CFI-42: 0.1 percent by weight. All these additives are currently being used in commercial diesel fuel.

Table 2 summarizes the results of complete ASTM fuel tests on #2 fuel oil, the pure soyates, and the soyates with additives. These tests were performed by Petroleum Research Division Farmland Industries, Kansas City, Missouri, with the exception of cetane number, which was done by Dresser Industries' Waukesha Engine Division.

The soyates had cetane numbers higher than the #2 fuel although the additives did not improve the rating greatly over the pure soyate. The CFI-42 additive did lower the cloud point for the soyates; however, it appeared that problems with jelling will occur as the fuel temperature approaches 0°C. A major cause for concern is the 16-hour gum test, which indicates that the soyates are much more susceptible to gum formation problems than diesel fuel.

TABLE 2.--ASTM Fuel Properties for Diesel Fuel and Soybean Oil Esters

Test Property	ASTM NO.	#2 Ref. Diesel Fuel	Methyl Soyate	Methyl Soyate with additives	Ethyl Soyate	Ethyl Soyate with additives	Butyl Soyate	Butyl Soyate with additives
Visc. @ 40°C (cSt)	D445	2.39	4.08	4.14	4.54	4.59	5.24	5.21
Cetane No. *	D613	45.8	46.2	48.7	48.2	49.0	51.7	54.0
Cetane index	D976	46.0	***	***	***	***	***	***
Higher Heating Value (MJ/kg)	D240	45.2	39.8	39.9	40.0	40.0	40.7	40.6
(MJ/l)		38.3	34.6	35.3	35.2	35.3	35.6	35.6
@ 15.6/15.6 °C								
Specific Grav.		.847	.884	.887	.881	.882	.876	.876
API Grav.	D287	35.5	28.4	28.1	29.1	29.0	30.1	30.0
Distillation	D86							
50% pt °C		258	336	336	336	337	352	353
90% pt °C		296	342	347	344	351	364	369
Cloud pt. °C	D2500	-19	2	1	1	-2	-3	-4
Pour pt. °C	D97	-23	-1	-4	-4	-7	-7	-7
Flash pt. °C								
Clev Open Cup	D92	92	171	166	174	163	185	179
PM Closed Cup	D93	78	141	135	160	157	157	121
H ₂ O & Sediment (% vol)	D1796	trace	trace	trace	trace	trace	trace	trace
Sulfur(% mass)	D129	.25	.01	.01	.01	.01	.01	.01
Cu. Corrosion 98.9 °C	D130	1-a	1-a	1-a	1-a	1-a	1-a	1-a
Ash(% mass)	D482	.025	<.01	.01	.01	.01	.01	<.01
% Ramsbottom Carbon Residue	D524	.14	.30	.25	.69	2.19	2.21	2.55
Gum No.	***	6.6	16400	15500	19200	18400	17900	13400
Color	***	L3.0	L1.5	L1.5	L1.0	L1.5	L1.0	L1.0
Color	D1500	L2.0	L2.0	L2.0	L2.0	L2.0	L3.0	L2.5

* Cetane tests ran by Waukesha, all others by Farmland Industries

** off scale

*** 16-hour accelerated Williams Pipeline Test

ENGINE PERFORMANCE

A John Deere 4239TF direct injection, turbocharged diesel engine was used as the test engine. It is a four-cylinder unit with a bore of 106 mm, a stroke of 110 mm, and a displacement of 3.917 liters. The compression ratio is 16.2:1, and the Roosa injector pump is a distributor type pump. Before any startup, the engine was "blueprinted" with measurements made on critical engine components by Farmland Industries Petroleum Research Division at Kansas City, Missouri.

The maximum brake power output at full rack for all the fuels fell between 2450 and 2500 rpm. The reference fuel and the butyl soyate were nearly identical in maximum power output while the methyl soyate showed a 2.5 percent drop in maximum power compared to the reference fuel. The ethyl soyate was the lowest with a 4.0 percent decline in maximum power compared with diesel.

The methyl and ethyl soyates had about an 11-percent lower heating value than the diesel fuel on a mass basis while the butyl soyate was about 10 percent less. Increased fuel consumption on a mass basis by the soyates explains part of the discrepancy between the heating value and power differences. On a volume basis, the methyl and ethyl soyates contain about 8 percent less heat than the reference fuel, and the butyl soyate contains about 7 percent less.

Brake thermal efficiency was calculated on the basis of lower heating value, indicating very little difference in the efficiency of the various fuels.

In general, the soyates displayed engine performance characteristics very similar to diesel fuel. The small differences were mainly a result of the lower heating value of the soyates and their greater density. The engine performed smoothly in all the tests and exhibited no starting problems. There was no audible knock as expected from the high cetane numbers for the esters.

EMISSIONS

The specific emissions of CO, CO₂, and unburned hydrocarbons were very similar for the four fuels.

Nitrous oxide measurements revealed major differences between the soyates and the diesel fuel. The soyates' NO emissions ranged from two to five times that measured for the diesel fuel. The methyl soyate produced the highest levels, followed by the butyl soyate. The exhaust gas temperatures followed the same order as the level of NO emissions among the fuels. However, the exhaust gas temperature differences between the fuels of 20 to 70 °C does not explain the large differences between NO emissions. All of the fuels gave lower values at 2200 rpm than at 1500 rpm, which was expected due to the reduced residence time of the fuel in the combustion chamber at the higher speed setting. Higher combustion temperatures at 2200 rpm did not seem to occur as revealed by the exhaust gas temperatures at the two speeds and the evident reduction in NO levels at 2200 rpm. This is most likely due to the lower air-fuel ratios that were measured during the higher speed tests.

ENGINE WEAR AND DEPOSITS

Indication of engine wear was monitored by analysis of the lubricating oil for wear-metal levels. Wear-metal levels for the soyate fuels were considered to be normal throughout the 200-hour test.

The lubricating-oil viscosity was monitored over the 100-hour oil change interval. For all the fuels, the initial shear of the oil caused a rapid drop in viscosity during the first 10-20 hours. In the case of the reference fuel, the viscosity then stabilized at about 103 cSt. For all the soyates, however, the viscosity continued to drop for the entire 100 hours, which suggests that more oil dilution was taking place. This could eventually lead to oil thickening as the antioxidant additives in the oil become depleted. However, this did not happen during the normal oil-service interval.

Conclusive evidence of engine wear can only be established by physical measurement of the various parts, and there was no notable difference between the wear patterns of the ester fuels and the reference fuel. In all cases, the honing marks in the liners were still clearly visible, as were the machining marks on the pistons. The valve stems had a slight polish, and the valve seat contact area was just starting to show.

TABLE 3.--John Deere 4239TF Engine Deposit Inspection for each 200 hr Test

	Diesel	Methyl	Ethyl	Butyl
Pistons -Deposit Rating-*				
% Top Groove Fill	0.0	17.5	0.0	75.0
2nd Groove, % Carbon Fill	0.0	0.0	0.0	0.0
Oil Groove, & Cover (% clean)	100.0	33.8	100.0	86.3
very light amber laquer (%)	0.0	66.2	0.0	2.5
light amber laquer (%)	0.0	0.0	0.0	11.2
Top Land % Med. Carbon	7.0	0.0	0.0	0.0
2nd Land % Carbon + Black Laq.	0.0	0.0	0.0	0.0
Wtd. Total Demerits (Grooves)	42.4	56.6	45.3	71.5
Wtd. Total Demerits (Lands)	4.8	7.8	5.2	8.8
Total Piston WTD (Avg.)	47.2	64.4	50.5	80.3
Valves -CRC Rating-*				
Exhaust Valves	9.0	9.2	9.5	9.2
Intake Valves	7.2	7.8	8.4	8.7

* Piston WTD rating increases with increased deposits while CRC ratings decrease with increased deposits.

The injector tips were as deposit free as in the diesel test for all the soyate fuels. There were no obstructed orifices and the spray patterns were unaffected. Cracking pressures declined by an average of about 603 kPa for the ethyl soyate as opposed to about 1535 kPa for the reference fuel test and about 1078 kPa and 819 kPa for the methyl soyate and butyl soyate, respectively. The lower cracking pressure decrease for the ethyl soyate was not an abnormal condition as injectors tend to wear less rapidly as hours are accumulated (injectors were not replaced after the 200-hour diesel fuel baseline test).

The injector pump calibration was checked before the diesel test and after the ethyl soyate test. The pump delivery did not change significantly, indicating that no abnormal wear had taken place.

CONCLUSIONS

1. Ethyl, methyl, and butyl soyates with commercial diesel fuel additives have fuel properties that compare very well with diesel fuel. The high gum content, however, is undesirable from the standpoint of fuel-filter

clogging and long-term storage.

2. The pour point improver provided a significant drop in the ethyl soyate pour point, meriting further experimentation with different treatment rates. The high flash points of the soyates make them safer to handle than diesel fuel.
3. The transesterification process raises the cetane number of the vegetable oil to levels higher than diesel values.
4. The ASTM fuel tests provide significant insight into the potential of a candidate compression-ignition fuel.
5. Engine performance for the soybean esters does not differ greatly from diesel fuel performance. A slight power loss, combined with an increase in fuel consumption, was experienced with the soyates. This is mainly attributed to the lower heating value of the soyates.
6. Emissions were similar for all fuels. Hydrocarbons for the soyates were lower than for diesel while nitrogen oxide emissions were higher.
7. Engine wear for all fuels was found to be normal after the 200-hour tests. Deposits were comparable with respect to amount but slightly different in color and texture. Injection equipment tests showed no differences among the four fuels.
8. The ethyl, methyl, and butyl soyates could be used as alternative fuels on a short-term basis, provided certain fuel quality standards are met. The gum problem needs to be solved to eliminate fuel-filter clogging and problems relating to storage.

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PERFORMANCE AND DURABILITY EFFECTS OF SOME HYBRID FUELS

C. E. Goering and B. Fry^{1/}

ABSTRACT

Two hybrid fuels and No. 2 diesel fuel were burned in DI diesel engines to compare effects on engine durability. One hybrid fuel was a solution of soybean oil, 1-butanol, and diesel fuel. The other hybrid was a micro-emulsion of the preceding components plus 190-proof ethanol. The engines were run for 200 hours on each fuel at loads and speeds prescribed by the EMA (Engine Manufacturer's Association) cycle. The hybrid fuels produced less wear than diesel fuel, but carbon deposits with the hybrids were heavier on the intake valves, injector tips, and the tops of the cylinder liners.

INTRODUCTION

Renewable fuels derived from vegetable oils can provide good engine performance in the short term (Barenescu, et al., 1982; Goering, et al., 1982a; Peterson, et al., 1981; Varde 1982). In more extended operations, the same fuels can cause excessive carbon and lacquer formations, degradation of engine performance, and actual engine damage. Therefore, the objective of this research was to evaluate hybrid fuels comparatively with No. 2 diesel fuel by burning them in engines operating with load-speed cycles recommended by the EMA (USDA 1982). The duration of the EMA test is 200 hours of actual running.

EXPERIMENTAL

A computer-based controller was developed to carry out the EMA cycle automatically. The system was designed to interrupt testing if malfunctions occurred or if a 10-percent power loss occurred. The engine was instrumented for measurement of critical temperatures. Fuel consumption and blowby rates were also measured.

Two identical Deere, Model 4219D, 3,859L, DI engines were used. They were rated at 41.8 kW continuous at 2200 rev/min and had compression ratios of 16.3:1. Both engines were fitted with turbochargers prior to the tests. One engine was labelled A and the other B for convenience in referencing. An AW Model 400 prony-brake dynamometer supplied load for the engine under computer control.

^{1/} Goering is a professor and Fry is an academic professional in the Agricultural Engineering Department, University of Illinois, Urbana, Ill. 61801.

Compositions of all fuels are given in table 1 and key fuel properties are given in table 2. The baseline No. 2 diesel fuel is identified as D2. A nonionic microemulsion developed at the USDA laboratory in Peoria, Ill., identified as SNI. A triblend fuel developed at The University of Illinois is identified as UTB.

Table 1.--Composition of fuels

Component	Composition, %		
	D2	SNI	UTB
No. 2 diesel fuel	100	50	33
Degummed, alkali-refined soybean oil	0	25	33
190-proof ethanol	0	5	0
1-Butanol	0	20	33
Cetane improver	0	0	1

Table 2.--Properties of fuels

Property	D2	SNI	UTB
Viscosity @ 38°C, mm ² /s	2.82	4.03	4.86
Stability @ 5°C, hours	∞	> 24	∞
Higher heating value, kJ/kg	45529	41263	40224
Stoichiometric air fuel ratio	14.6	13.1	12.7
Flash point, °C	62.2	28.3	38.9
Ramsbottom carbon residue	0.01 ^{1/}	0.14 ^{2/}	0.17 ^{2/}
Cetane No.	51.4	34.7	38.9

^{1/}Percent of 10% residium.
^{2/}Percent of whole sample.

Typical procedure was to measure engine parts while rebuilding the engine with new parts at critical points. Following a break-in period, the EMA cycle was started, except that performance measurements were taken at 0, 105, and 200 EMA hours. Injection nozzles were bench tested before and after the tests. The lubricating oil was sampled daily for viscosity changes and at 50-hour intervals for wear metals.

RESULTS AND DISCUSSION

The engines completed the 200-hour tests on all three fuels without replacing any engine parts. Initial engine performance on D2 baseline fuel was essentially reproduced after 105 and 200 EMA hours.

Engine performance on SNI fuel is shown in figure 1. Size of fuel injections was unaffected by accumulation of EMA hours, but an efficiency loss of approximately 5 percent after 200 hours caused a corresponding 5-percent loss in BMEP (Brake Mean Effective Pressure) and power.

Figure 2 shows performance of the UTB fuel. There was no noticeable change in any of the performance parameters with accumulation of EMA hours.

Performance of the injector nozzles was bench tested and the results are summarized in table 3. Test equipment was not available for initial tests of nozzles used with D2 fuel. An extra test of nozzles used for UTB fuel was done at 120 EMA hours when the engine suffered a 10-percent power loss. The power loss was subsequently traced to a dynamometer malfunction, and the nozzles were re-installed without disturbing the carbon deposits on them.

Table 3.--Performance summary of injection nozzles

Parameter	EMA hours	D2		SNI		UTB	
		AVE	SD	AVE	SD	AVE	SD
Nozzle opening pressure, MPa	0	-	-	21.5	0.15	21.6	0.15
	120	-	-	-	-	21.9	0.26
	200	21.0	0.33	20.5	0.14	20.4	0.67
Orifice size, m	0	-	-	273	6.19	272	5.61
	120	-	-	-	-	268	4.06
	200	261	6.64	189	97.9	245	65.9

Accumulation of EMA hours had little effect on nozzle-opening pressures. The nozzles were subsequently disassembled and the needles were free and clean. Carbon deposits were heavier on the nozzle tips used 200 hours with the hybrid fuels and tended to form trumpets around the orifices. The trumpets partially obstructed one of the orifices on each of the nozzles used with SNI fuel, as indicated by the reduced average orifice diameter and greatly increased standard deviation (table 3). Only one orifice on one nozzle was obstructed for the engine running 200 hours on UTB fuel. The 5-percent reduction in thermal efficiency after 200 hours on SNI fuel (fig. 1) was probably caused by the carbon obstructions on the nozzle orifice tips.

The engines that ran on hybrid fuels had much heavier carbon deposits on the liner tops and removal of pistons past the carbon bands was difficult. The hybrid fuels also produced heavier carbon deposits on the intake valves (table 4). The carbon was in the form of flaky deposits on the intake valve tulips. Intake valve stems were clean in the guide travel area for all fuels. All exhaust valves had light carbon deposits below the guide travel area. The exhaust valves from the engines running on hybrid fuels had varnish streaks extending to the top of the guide travel area. A dome of carbon was found on the tops of the exhaust valve guides of the engines running on the hybrid fuels.

Table 4.--Average weights of carbon deposits on valves

Fuel	Milligrams of carbon on			
	Exhaust valves		Intake valves	
	AVE	SD	AVE	SD
No. 2 diesel	75.5	20.5	88.9	15.5
Shipp nonionic	72.9	10.4	308.3	120.4
UIUC triblend	71.5	41.9	404.3	137.0

Carbon and lacquer deposits on the pistons were rated by Lubrizol Corporation. The overall demerit ratings were 351 for the engine running on D2 fuel and 418

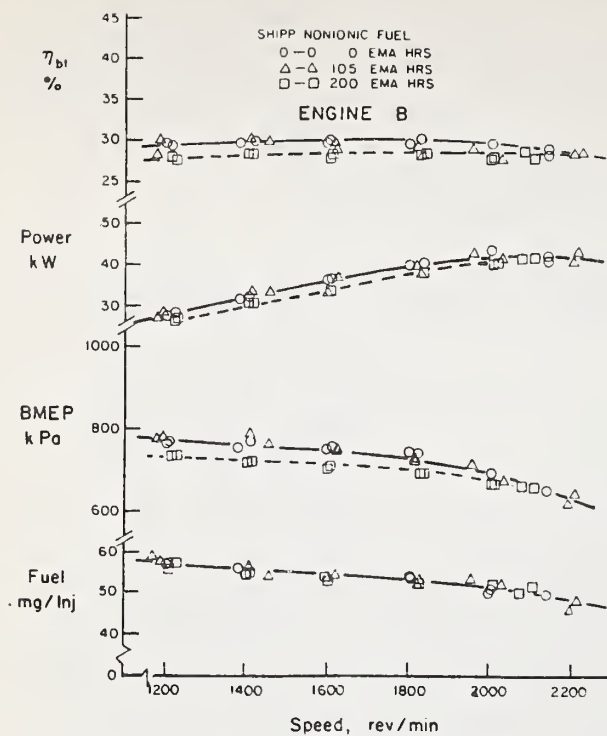


Figure 1.--Performance of SNI fuel.

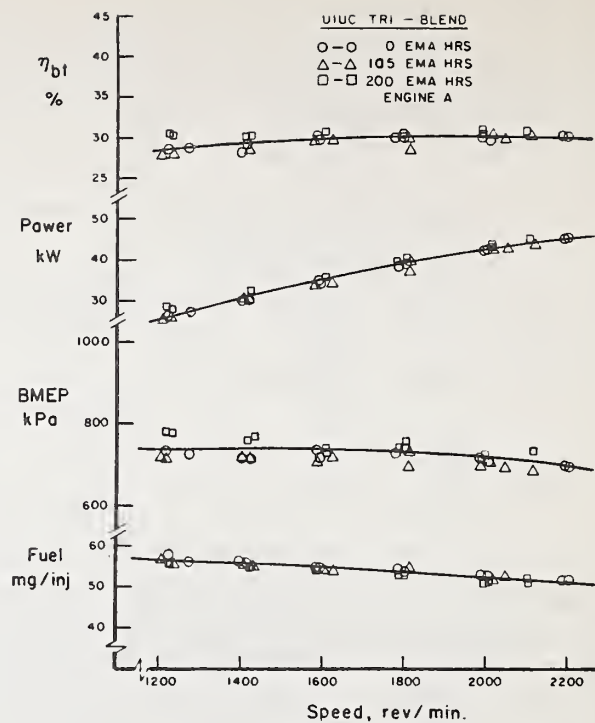


Figure 2.--Performance of UTB fuel.

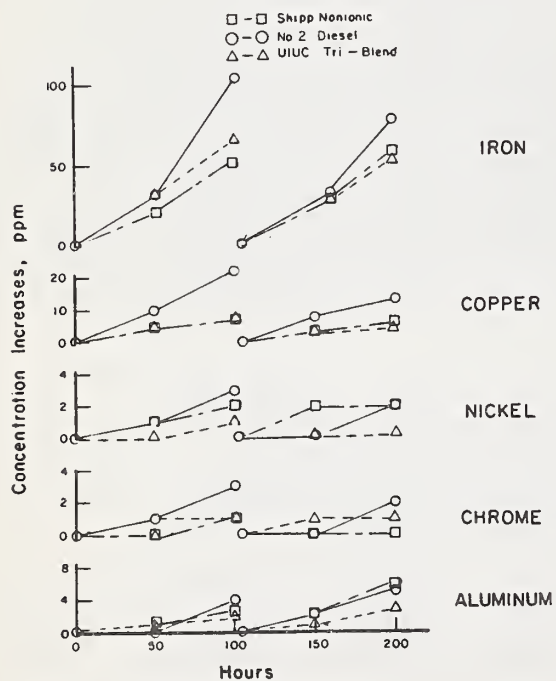


Figure 3.--Wear metals in oil.

for the engine running on SNI fuel. Lubrizol judged the deposits as acceptable on both sets of pistons. Ratings are not yet available for the pistons used with UTB fuel.

Average daily consumption of lubricating oil is shown in table 5. For unknown reasons, less lubricating oil was consumed by the engines burning the hybrid fuels. Viscosity of the lubricating oil (at 99°C) was checked daily, and it changed less than 10 percent over the 200-hour tests of the hybrid fuels.

Table 5.--Average daily consumption of lubricating oil

Time period (oil was changed @ 115 hours)	Average daily consumption, mL/hour with:		
	D2 fuel	SNI fuel	UTB fuel
First 100 hours	51.5	1.3	14.9
Second 100 hours	30.7	28.1	4.4

Figure 3 shows increases in wear metals in the lubricant during the tests. The hybrid fuels generally caused less wear than diesel fuel. This finding was substantiated for the rings and bearings by weighing metal loss during the tests.

When judged against criteria established by the EMA, both hybrid fuels were considered to pass. The SNI fuel was a marginal pass because performance had degraded approximately 5 percent at the end of 200 hours.

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ENGINE TESTS--MISCELLANEOUS

RAPID IGNITION QUALITY TESTING

R.R.M. Johnston and K.J. Harrington^{1/}

ABSTRACT

Twenty-seven experimental fuels were tested by throttling to misfire in two single cylinder production engines. Oils of cotton, sunflower, soya, and rapeseed gave the same ranking order in a direct injection (DI) and an indirect injection (IDI) engine. The ranking was similar to that obtained by other workers using conventional test methods. Methyl, ethyl, propyl, and butyl esters of a number of seedoils also showed similar behaviour patterns in both engines, a direct relationship being established between this ranking and iodine number. The relationship of the method to the standard ASTM D-613 procedure is discussed.

INTRODUCTION

The present work was carried out as part of CSIRO Project Crop-Fuel. The primary aim was to provide early fuel-screening information to guide research at the Divisions of Chemical and Wood Technology, and Plant Industry. A test relevant to production engines was required, but only small quantities of fuel (ca 300 ml) were available from bench preparation. The simple method of assessing ignition quality by engine throttling to misfire (1) was considered appropriate because:

- (a) Any single cylinder engine may be used,
- (b) No sophisticated measuring equipment is necessary,
- (c) Only small quantities of fuel are required, and
- (d) Being rapid, the engine is not fouled, even with poor fuels.

This method is currently incorporated in a British Institute of Petroleum standard (2) but is no longer widely used. However, it was widely reported (1,3,4,5), acclaimed to be reproducible, and gave a direct relationship with the CFR fixed, 13°-delay method for petroleum fuels (3).

EXPERIMENTAL

Method

The engine air intake was connected to a surge tank of capacity approximately x100 times the swept volume of the cylinder. Air was admitted through a stopcock, which was closed rapidly by hand. The running engine evacuated the tank until the mass of air drawn into the cylinder at each stroke became so low that misfire occurred. The test criterion was the

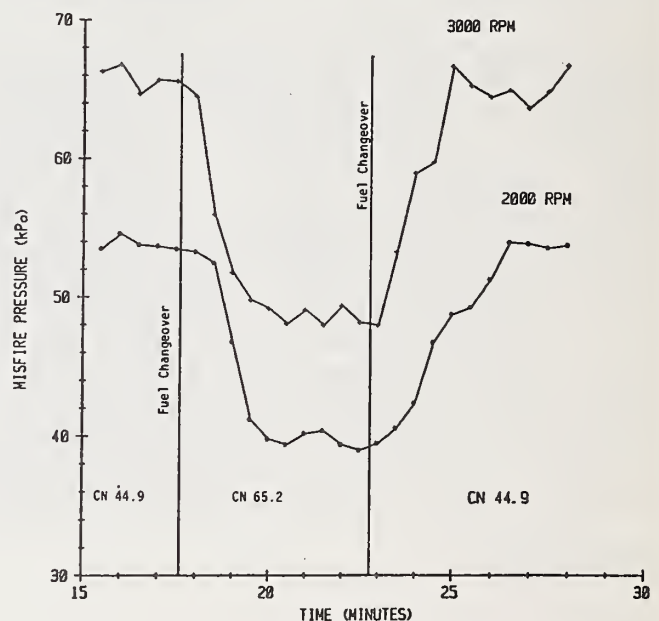
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reduction in intake pressure, measured by a transducer mounted in the tank wall, that an experimental fuel could tolerate to the point of misfire. The first misfire was detected by a second pressure transducer placed in the exhaust manifold. The regular exhaust pressure waves were displayed on a CRO. The point where this wave amplitude fell to zero agreed well with the first appearance of white smoke used earlier (1,2,4,5).

Tests were done at 2000 rpm and 3000 rpm in the DI engine and at top speed (2000 rpm) in the IDI engine (see next section). Although misfire pressure did not change appreciably with engine load, misfire was better defined at lower loads; 2.5 Nm (ca 10 pct maximum rated load) was used throughout.

Experimental fuels were run by gravity from a 100-ml glass burette, through a three-way, teflon-lined valve, directly to the injection pump. This minimized the dead volume of the fuel feed system. Prior to testing, the engine was warmed up on distillate and then run on the test fuel just long enough to flush the feed lines. Preliminary work showed that three to four minutes was required, depending on the speed and load (fig. 1). Each batch of experimental fuels was tested with the reference fuels in randomized order. Five successive misfire pressures were averaged for each test condition. This procedure was duplicated whenever more than 150 ml of fuel was available (8).

Fig. 1. Method used to determine time required for fuel changeover. Misfire pressure (absolute) measured at 30 sec. intervals. DI engine. Load 2.5 Nm.



Engines and Equipment

Engine specifications are given in the table. In both engines, injection timing was operated by the standard fixed cam. Details of dynamometers, engine run-in, and operation monitoring carried out to ensure consistent performance on distillate fuel have been described (6,8). Exhaust gas temperatures, not significantly different between the two engines at 2000 rpm, were elevated by about 50°C in the DI engine at the higher speed. This agrees with published calculations (7) of the effect of speed on peak gas temperature.

TEST ENGINE SPECIFICATIONS

	<u>DEUTZ</u> <u>FIL 208D</u>	<u>KUBOTA</u> <u>ER 40-N1</u>
COMPRESSION RATIO	17	22
CAPACITY (cm ³)	413	331
POWER kW (continuous)	5.25 (3000 rpm)	3.7 (2000 rpm)
COOLING	air	water
SPILL TIMING ADVANCE	23° BTDC	19° BTDC
COMBUSTION CHAMBER	DI swirl recess in piston	IDI spherical pre-chamber

Fuels

Secondary reference mixtures were prepared from two proprietary kerosenes, T17 and U10, supplied by Phillips Chemical Co., Bartlesville, Okla.,. Measurements were also made with the primary standard, cetane. In addition, a single batch of commercial distillate was used to show whether consistent results could be obtained with a conventional fuel.

The series of aliphatic alcohols, methyl, ethyl, n-propyl, iso-propyl, and n-butyl, was used (9) to prepare esters from commercial fatty acid mixtures as well as from sunflower oil. In addition, methyl esters were prepared from peanut, rapeseed, and castor oil. These fuels were triply distilled and did not require filtering. Chemical compositions have been given elsewhere (8,9).

Four seedoils, cottonseed, soyabean, sunflower, and rapeseed, were supplied by Repco Engine Parts (10). These fuels were vacuum filtered into the burette through a Whatman GF/A fibreglass filter having nominal pore size of 1.5 µm.

ENGINE TEST RESULTS

Reference Fuels

Air intake pressures necessary to cause misfire with the reference fuels in the DI engine are shown for the two engine speeds in figure 2. The higher the cetane number the lower the intake pressure necessary to cause misfire, in accord with earlier work (1). Misfire occurs at a smaller departure of the intake pressure from atmospheric (i.e. at a higher pressure) at the higher speed. The misfire pressure for cetane was found to be the same at both speeds. Because the shift of misfire pressure of distillate with changing speed is similar to that of the reference mixtures, the cetane ranking, which may be ascribed to distillate from the figure, is independent of engine speed, within the limits of reproducibility. Reduction of intake pressure increases ignition delay (11). Higher speed is more prone to misfire (i.e. smaller pressure departure from atmospheric) because the expansion stroke commences to cool the charge before effective combustion can occur. Cetane, with the smallest ignition delay, fires equally well at 3000 rpm, in the reduced time available, as at 2000 rpm.

The plot of misfire pressure versus cetane number of the reference fuels in the IDI engine at 2000 rpm was similar to the lower curve in figure 2. However, because of differences in engine design, similar results obtained at the same speed may not be directly comparable.

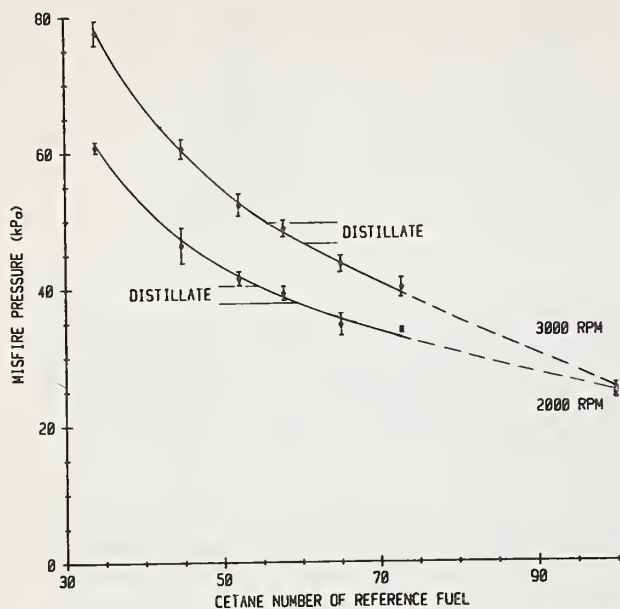
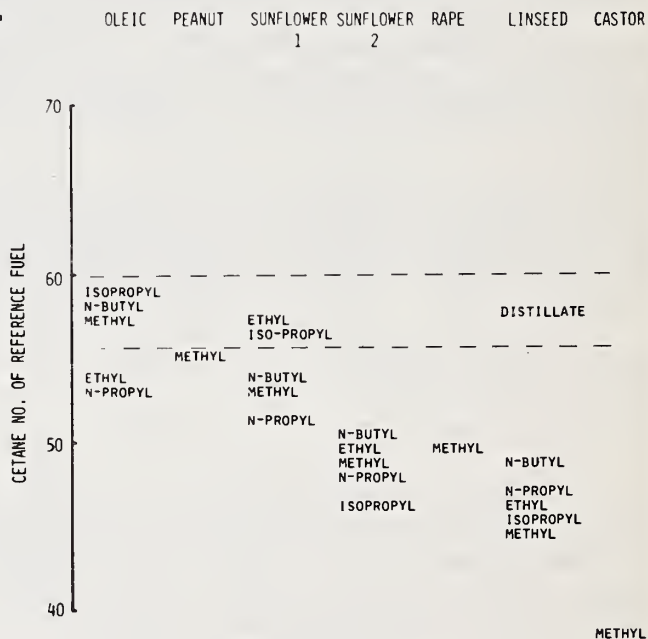


Fig. 2. Misfire pressure (absolute) of reference fuels in DI engine. Load 2.5 Nm. The error bands represent $\pm 2\sigma$ for five successive misfire readings.

Fig. 3. Cetane ranking of esters run in DI engine. Speed 2000 rpm. Load 2.5 Nm.



Ignition Quality Ranking of Ester and Seedoils

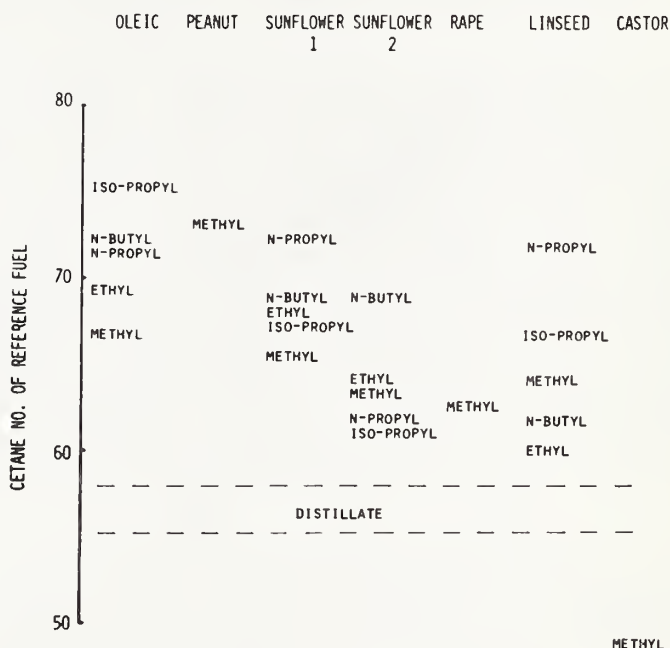
Esters. The cetane ranking data obtained in the DI engine at 2000 rpm are shown in figure 3. The esters are arranged in columns, according to the source of the fatty acid constituent (i.e. seedoil or commercial fatty acid mixture). The level ascribed to the esters in each column is derived from their performance in the throttling test. The horizontal broken lines represent the uncertainty ($\pm 2\sigma$) in the cetane ranking found for distillate. Unlike distillate, speed had a significant influence on the

ignition behaviour of the esters. The misfire pressures of both the esters and the reference fuels were raised by increasing speed, but those of the esters were raised less. Therefore, the cetane ranking for the esters was raised (generally by about 5 units), in comparison with distillate by changing the speed in the DI engine from 2000 rpm to 3000 rpm (8).

The methyl esters of peanut, rape, and castor oil were included to broaden the scope of the data. The ignition behaviour of the methyl ester of castor is singularly poor in this test. This is in accord with the findings of earlier workers (12) who reported direct measurement of ignition delay.

Figure 4 shows that the cetane ranking of the esters in the IDI engine is appreciably higher than in the DI engine. Despite the movement of the cetane values of the esters up and down the scale, the ranking of the series across the columns has been maintained. On the other hand, the order of the individual esters seems quite random, in accord with the likely detection limits of the method ($2\sigma = \pm 1 \frac{1}{2}$ cetane number units (8)).

Fig. 4 Cetane ranking of esters run in IDI engine. Speed 2000 rpm. Load 2.5 Nm.



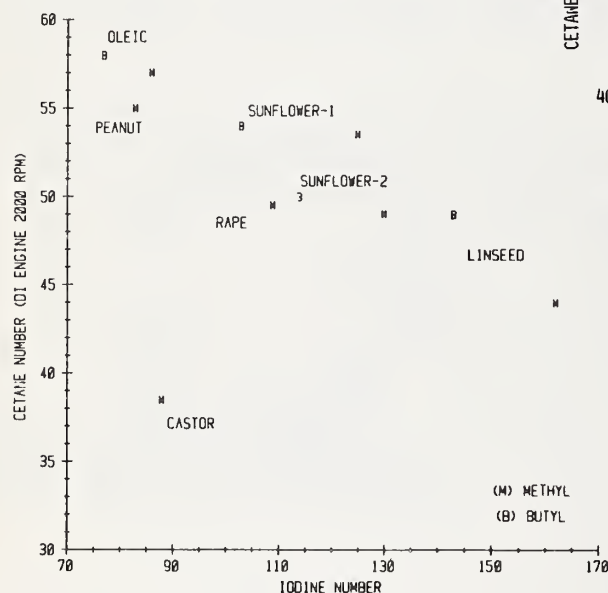
Seedoils. Figure 5 shows the cetane ranking of the four seedoils. Again, the values obtained in the IDI engine (left) are appreciably higher than in the DI engine (right). Apart from rapeseed in the latter, a consistent pattern and ranking order is obtained in both engines. This ranking, cottonseed, soyabean, sunflower, and rapeseed, is similar to their order of performance in much more extensive testing in a different DI engine (10).

UNSATURATION OF CHEMICAL BONDING OF ESTERS

The iodine uptake of the methyl and butyl esters was determined (Amer. Oil Chem. Soc. Method Cd 1-25) to show the degree of unsaturation in the fatty acid chains derived from the seven sources. Figure 6 shows a direct relationship between iodine number and cetane ranking (from fig. 3) obtained

by throttling. In each case the butyl esters have a lower iodine number than their methyl counterparts. This occurs because the average molecular weight of the former is ca 15 pct higher. Therefore, the number of unsaturated bonds per unit weight of material will be proportionately less. The methyl ester of castor oil has a much lower cetane ranking than its degree of unsaturation would indicate. This is due to the major constituent ricinoleate having a (hydroxyl) side branch, a structure that gives poor compression ignition behaviour, apart from considerations of unsaturation (9).

Fig. 5. Cetane ranking of seedoils run in IDI engine (left) and DI engine (right). Speed 2000 rpm. Load 2.5 Nm.



DISCUSSION

The standard ASTM D-613 procedure, using a CFR engine, compares the compression ratio necessary to produce the same ignition delay for all fuels. Injection is made at a crank angle of 13° BTDC, allowing 2.41 ms for ignition to occur, at TDC, at 900 rpm. Although much diesel technology is based on it, 2.41 ms is, clearly, an arbitrary criterion and may be too long for unconventional fuels intended for high speed engines.

When engine throttling is carried out, the reduction of intake pressure produces a continuously increasing ignition delay. Eventually, the expansion stroke reaches a point where the charge starts to cool, before combustion can be effective, and misfire occurs. The fact that better quality fuels will tolerate lower intake pressures, before misfire occurs, is analogous to the lower compression ratios associated with higher cetane numbers in the CFR engine (13). Although the throttling test actually

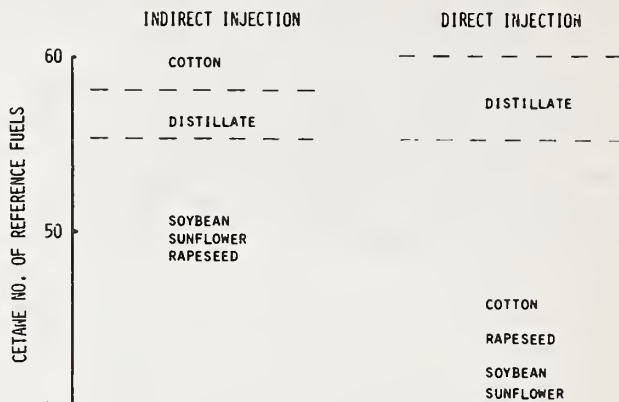


Fig. 6. Relationship between cetane ranking (from fig. 3) and degree of unsaturation as measured by iodine number.

compares the ignition behaviour of fuels at different combustion chamber pressures, this may create less uncertainty than the change in combustion chamber shape, which accompanies adjustment of compression ratio in the standard (ASTM D-613) method.

The factors that increase ignition delay in the throttling test are low air intake pressure and temperature, low compression temperature, low fuel temperature, and poor ignition quality (low cetane rating) (1). Higher speeds allow less time for combustion processes and are, therefore, less tolerant to reduction of intake pressure and increase of ignition delay. Where volatility of a fuel is relatively low (e.g. esters and seedoils) in comparison with the petroleum derived reference fuels, cetane ranking may improve at higher speed due to the higher compression temperatures that occur (7). This effect may override the reduced time available for ignition. At equal intake pressures, it may be expected that an engine with higher compression ratio would develop a higher pressure at TDC. However, pumping and heat losses may have a counter influence. Injection timing is an additional complicating factor, which would affect the time available for ignition before expansion and cooling can cause misfire.

Engine throttling data cannot readily be compared with conventional cetane number data. Rather, throttling results should be regarded as providing a measure of ignition quality under specific operating conditions in any given engine. Since the precise relationship between temperature of the charge and crank angle will depend on factors characteristic of the test engine (such as speed, heat loss rates, and injection conditions), even direct measurements of delay in an engine with variable injection timing (12) may also need to be interpreted with caution. The present work has shown that the ranking order of a variety of experimental fuels was consistent at different speeds and between two very different engine types. This indicates that the test provides reliable data, a contention supported by the fact that four seedoils were ranked in a similar order to that shown in much more extensive engine testing in a different engine.

CONCLUSIONS

1. The simple test of engine throttling to misfire has been adapted to provide an ignition quality ranking with smaller quantities (ca 100 ml), of scarce experimental fuels than have previously been reported.
2. Self consistent data have been obtained in a DI and an IDI single cylinder engine for four seedoils and for esters prepared from seven fatty acid sources, cetane ranking being related to iodine number.
3. The test showed differences in ignition quality between esters, derived from different seedoils, but differences between esters prepared from the one seedoil using a homologous series of alcohols (methyl to n-butyl) were small and not readily distinguished.
4. The ranking order of the four seedoils is in accord with much more extensive conventional testing of the same materials. A very poor ranking obtained for the methyl ester of castor oil is in accord with the results of others who measured ignition delay directly.
5. The ignition quality data obtained by the engine-throttling technique is proving useful as a guide to research directions in the production of experimental fuels from seedoils and esters.

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ENGINE EVALUATIONS OF LINSEED OIL AND DERIVATIVES

G. R. Quick, P. J. Woodmore, B. T. Wilson^{1/}

ABSTRACT

The work continuing at the Agricultural Engineering Centre Glenfield in vegetable oil fuels has led to the identification of linseed oil as a very poor fuel and therefore one that would be most needful of modification before it could be seriously considered as a diesel fuel substitute or extender. Results of the 1000 hour test on linseed oil methyl ester in a direct injected engine are reported.

Indirect injected engines have been reported elsewhere as being capable of operating on lower quality fuels. Results of tests on identical engines of DI and IDI configuration operating on straight linseed oil and blends are reported.

^{1/}Quick is director of Agricultural Engineering, Woodmore is technical officer, and Wilson is senior technical officer at the Agricultural Engineering Centre, Glenfield, N.S.W.

LONG-RANGE ENGINE TESTS USING CANOLA OIL AS A FUEL

R. C. Strayer and W. K. Craig^{1/}

ABSTRACT

A two-cylinder direct injection engine, burning diesel fuel in one cylinder and canola oil, methyl ester, or rapeseed oil in the other cylinder, was used to compare cylinder deposits in 300-hour test cycles. Another two-cylinder engine was operated for 200-hour test cycles to compare lubricating oil deterioration, engine wear, and exhaust emissions when burning the same fuels. Results of the tests were not encouraging for long-term use of these fuels.

INTRODUCTION

The Canadian Prairie Provinces, and Saskatchewan in particular, are major producers of rapeseed and its low erucic acid successor, canola. When it was decided to pursue a research program to investigate alternate diesel fuels, these were the sources of the oil to be used. The program, funded by Agriculture Canada, was carried out in two phases. Phase one, which included a literature review, economic study, and preliminary engine testing, was completed in September 1981 and was reported on at this meeting two years ago and in Fargo in 1982. The second phase ran from December of 1981 to March of 1983 and involved more exhaustive and long-term engine testing to study combustion chamber deposits, lubricating oil deterioration, and exhaust emissions. The three groups that cooperated in this project were the Agricultural Engineering Department, University of Saskatchewan, the Saskatchewan Research Council, and the POS Pilot Plant at the University.

SUMMARY OF PHASE TWO STUDIES (Zoerb, 1983)

During Phase one, two engines were used--a two cylinder Petter diesel and a six cylinder turbocharged John Deere engine--and were run for only short tests. Longer test periods in the second phase required some revisions to test procedure. Because of the cost and limited availability of methyl ester, it was not practical to run two-to three-hundred hour tests on the John Deere engine, which consumed about forty liters of fuel per hour at full load. Thus all tests were conducted on two Petter engines, and two test procedures were developed, one to study cylinder deposits and the other to look at lubricating oil dilution and exhaust emissions.

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CYLINDER DEPOSIT STUDY

For this study, the engine's fuel system was altered so that one cylinder was run on diesel fuel and the other on the fuel to be compared. In this way, operating conditions could be controlled so that variables such as load, coolant temperature, and so on would be the same for both cylinders. As will be noted later, this method had one major limitation--the lubricating system could not be split, and the sharing of this system apparently upset the test results in one instance.

The tests ran 300 hours, with one oil change at 150 hours. The engine was operated at 75 percent of full load and was checked daily to ensure that each cylinder was producing the same power. Three fuels were compared with diesel fuel.

Test #1-- Diesel Fuel Versus Canola Oil (Mechanically Expelled)

This test proceeded normally until about 260 hours, when some power loss was detected in the canola cylinder, and there was a noticeable increase in oil consumption. The test was completed, the engine dismantled, and the condition of the combustion chamber, piston, and piston rings were observed. Deposits in the canola cylinder were quite severe and included stuck piston rings. The deposits in the diesel cylinder were more severe than would be normal at 300 hours, probably due to the lubricating oil contamination from the seized piston rings in the other cylinder.

Test #2-- Diesel Fuel Versus Methyl Ester

Little difference could be noted in deposits between the two cylinders.

Test #3-- Diesel Fuel Versus R500 Rapeseed Oil (This oil was solvent extracted, refined and degummed)

Problems in engine performance developed quickly due to a severe deposit at the base of the injection nozzle in the R500 cylinder. The test was completed by removal of the injection nozzle at about 40 hour intervals to clear the deposit away.

Results of the test showed severe deposits in the R500 cylinders, with piston rings and ring grooves badly fouled, though no rings were stuck solid.

The deposit buildup around the injection nozzle was also experienced with the other Petter engine when burning the same R500 oil.

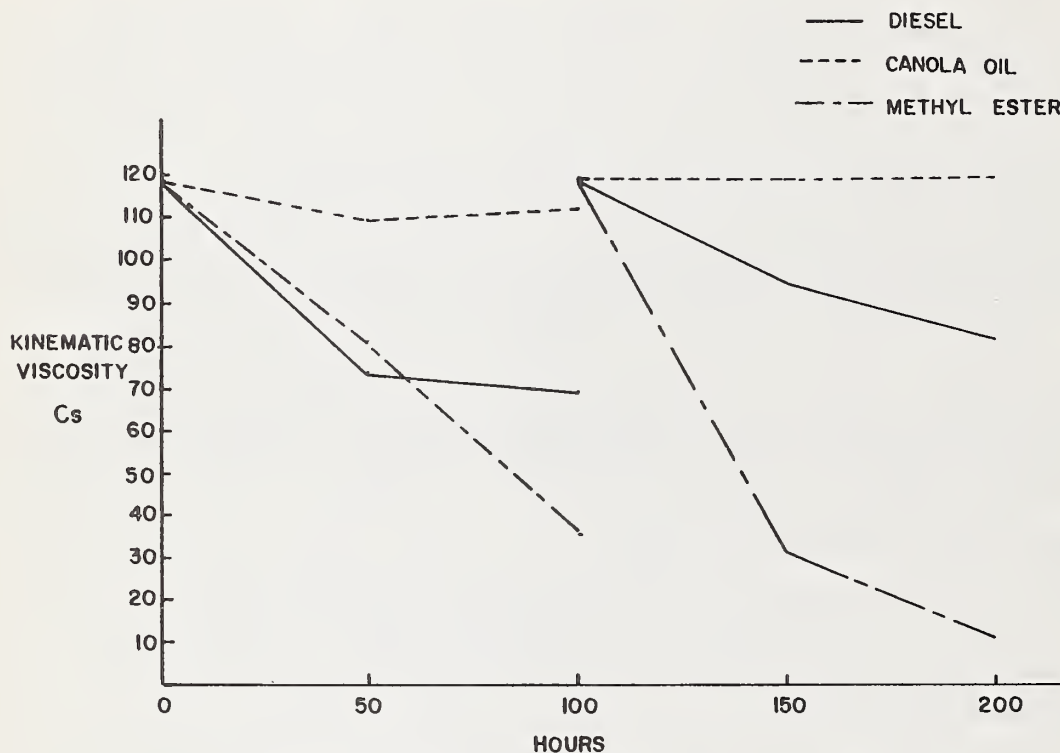
LUBRICATING OIL ANALYSIS

A second-two cylinder Petter engine was used to evaluate lubricating oil contamination while burning various fuels. The engine was run for 200 hours at about 80 percent of full load, with an oil change at 100 hours. Samples were taken at 50, 100, 150, and 200 hours when burning diesel fuel, canola oil, and methyl ester. (Tests with R500 oil as a fuel were abandoned due to severe

injector fouling.) The following tests were performed:

1. Kinematic Viscosity at 38°C (100°F). See figure 1.

Viscosity reduction was negligible when burning canola oil, moderate with diesel fuel, and severe with methyl ester. This would seem to signify the need for very frequent oil changes if the latter were used as fuel.



VISCOSITY CHANGE OF LUBRICATING OIL AT 100°F

Figure 1

2. Fuel Dilution

Fuel dilution when burning diesel fuel was higher than would be expected, possibly due to an engine malfunction during the first 100 hours of the test. Dilution with canola oil as fuel was high and, when burning methyl ester, would be considered completely unacceptable.

3. Wear Metals. See figure 2.

With the exception of copper and aluminum, the concentration of all wear metals were within acceptable limits. However, when either canola oil or methyl ester was used, there was a general increase in all wear metals, ranging from 30 percent to 730 percent, which would indicate more rapid engine deterioration.

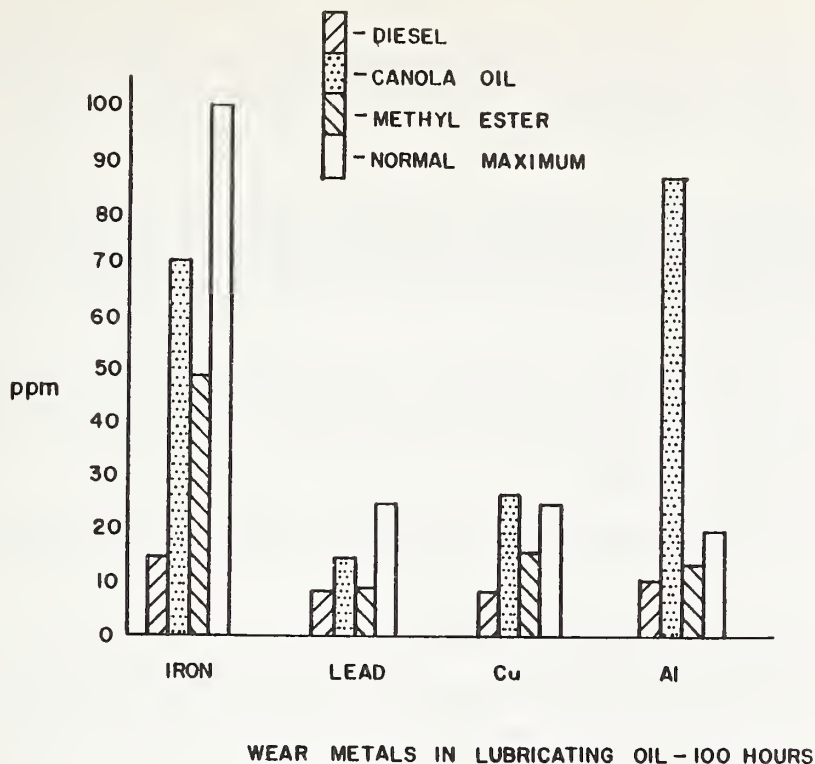


Figure 2

4. Oxidation and Thermal Contamination

Since benzene dissolves everything in the used oil but the nondispersed solids, while pentane dissolves everything but the nondispersed insolubles (including fuel soot and dirt), the difference when benzene insolubles are subtracted from pentane insolubles is a measure of oxidation resins (Georgi 1950). Some unexplainable discrepancies appeared in the results but, in general, the level of both pentane insolubles and benzene insolubles, while considered within acceptable limits by the lubricating oil manufacturer, was considerably higher when burning canola oil and methyl ester. The "pentane minus benzene" number is much higher for the oil when burning methyl canolate, indicating a higher level of oxidation resins. However, this same fuel produced an oil with a lower total acid number (TAN) than either diesel fuel or canola oil, and since this number, and the amount it changes, is also an indication of relative changes that occur in an oil under oxidizing conditions (ASTM D974-64), it appears that more complex reactions are occurring in the oil when vegetable oil fuels are being burned. These results are similar to those of other researchers such as Siekmann (1982) and indicate that the additive package present in engine oils may not be suitable for use when vegetable oils are used as fuels.

EXHAUST GAS ANALYSIS

Very comprehensive exhaust analysis methods were used to obtain emission levels while the engine was being operated for lubricating oil tests. Two separate experiments were conducted.

(a) During the 200-hour engine testing of the fuel systems, exhaust gas samples were withdrawn and analyzed for aldehydes, NO_x , CO, and CO_2 at 50-hour intervals. Results showed that no differences could be detected in the concentrations of these emissions as a function of time, but the type of fuel used produced differences.

(b) To ascertain the particulate emissions, the exhaust gas was sampled isokinetically with samples taken at various load levels. At the same time, the levels of aldehydes, NO_x , CO, and CO_2 were determined. The results of these tests at full load indicate that:

1. CO emissions with vegetable oil-based fuels were double those from diesel fuel.

2. CO_2 levels were about the same with all fuels.

3. Particulate emissions were 40 percent to 240 percent higher when burning vegetable oil-based fuels than when burning diesel fuels. Also, the methyl canolate produced much higher particulate emissions than the more viscous canola oil from which it was prepared.

4. Aldehyde levels were four to eight times higher with vegetable oils than with diesel fuel.

5. Vegetable oil fuels emitted lower levels of NO_x than diesel fuel. Varde (1982) reported similar results when comparing soybean oil with diesel fuel, and this would seem to indicate lower combustion temperatures.

CONCLUSIONS

All the objectives of the research into use of canola oil fuels could not be achieved due to reasons already explained. However, sufficient data were gathered to draw a number of conclusions, which in some instances were unique and in others offered comparison with work done by other researchers on other vegetable oils. The major conclusions to be drawn from this research are:

1. Canola oil is not a satisfactory fuel in a direct injection engine for continuous operation due to the serious deposits produced in the combustion chamber.

2. Conversion of canola oil to a methyl ester will reduce the problem with engine deposits.

3. Crankcase oil dilution and oxidation are more serious with canola oil-based fuels.

4. Higher than normal wear rates would occur in an engine burning canola oil or methyl ester.

5. Higher levels of aldehydes and particulates would be expected in the exhaust gases under full load conditions when burning canola oil or methyl ester.

6. Test work to this point has involved an unmodified engine using lubricating oil fabricated specifically for use with hydrocarbon fuels. Continued research is needed to assess engine modifications and different oil and fuel additives.

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SOYBEAN ESTER AS ALTERNATIVE DIESEL FUEL TESTED
IN DI ENGINE-POWERED VOLKSWAGEN TRUCKS

G.H.Pischinger, A.M.Falcon, R.W.Siekmann ^{1/}

ABSTRACT

Tests with straight methylester of soybean oil (MESO) in DI-engined VW 13-ton GVW trucks gave good performance, drivability, and consumption. High lubricating-oil dilution by unburned MESO in the unmodified DI engine demands a lube-oil drain at 20 per cent of the recommended period for diesel oil. There are two solutions to minimize the lubricating-oil dilution in order to permit reaching the recommended lube-oil drain period for diesel oil: minor engine modification, such as changes to the injector characteristics, or the use of a maximum of 30-per cent volume of MESO in the diesel oil.

INTRODUCTION

Numerous alternative fuels have been proposed in Brazil to reduce the demand for diesel oil. Both straight biomass fuels, such as alcohols and vegetable oils, and their mixtures with petroleum derivatives have been considered. Depending on the alternative fuel, different levels of engine modification may be required. Volkswagen, in Brazil, aims at an alternative that meets the following requirements: compatibility with the existing fleet; compatibility with the existing diesel oil distribution network; and total miscibility with diesel oil so as to permit gradual substitution in proportions differing from one region to another.

In this respect, vegetable oils show the highest potential among today's known biomass-based alternative diesel fuels, so we concentrated our work mainly on them. Running diesel engines on untreated vegetable oil, whether straight or in higher percentages blended into diesel oil, cause combustion chamber deposits (1, 2), which can be eliminated by using monoesters obtained by transesterification.

^{1/}Pischinger is manager of the Research Division, Falcon is manager of the Applied Research Department, and Siekmann is manager of the Research Department of Energy Technology and Alternative Fuels, Volkswagen do Brasil, S.A.

This paper reports part of Volkswagen's experience in using methyl ester of soybean oil (MESO) as an alternative test fuel in unmodified direct and indirect injection engines. The results with indirect injection engines are concisely presented. Two solutions, to improve the MESO combustion in direct injection engines are also discussed in order to minimize the excessive lube oil-dilution by MESO. Methyl ester of soybean oil was chosen because, at the moment, soybean is Brazil's main vegetable oil.

TEST ENGINES AND VEHICLES

Because the objective is to study alternative fuels for existing diesel engines, the vehicles and engines used in testing were regular production models. Testing was done on VW light-duty delivery vans and VW 13-ton GVW trucks. Engine specifications are:

	<u>VW-Light Delivery Van</u>	<u>VW 13-ton GVW Truck</u>
Manufacturer	VW	MWM(D-229-6)
Cylinders	4 in line	6 in line
Displacement	1588 cm ³	5883 cm ³
Bore/Stroke	76,5mm/86,4mm	102mm/120mm
Compression ratio	23	16
Injection pump	rotary	in line
Lube-oil drain period	7500Km	5000Km

TESTING FUELS

The methylester, obtained from degummed and neutralized soybean oil, is analyzed lot by lot for conformity with the specifications in table 1.

Table 1: Preliminary specification of methylester of soybean oil

	<u>Specified Value</u>	<u>Method</u>
Acidity (mgKOH/g)	max. 0.7	AOCS Cd 3a-63
Peroxide index (mEq/1000g)	max.30	AOCS Cc 07-25
Cloud point (°C)	max. 6	ASTM D-97
Water content (wt.pct)	max. 0,1	Karl Fischer
Kinem. viscosity(cSt at 40°C)	1,6-6	ASTM D-445
Density 25/4°C (g/cm ³)	0.8799-0.8820	ASTM D-1298
Soap content (ppm)	max.10	AOCS Cc 15-60
Triglycerides (wt.pct)	max. 0,5	TLC
Methanol (wt.pct)	max. 2	
Cetane number	45	ASTM D-613
Heating value (net.), (MJ/l)	38,5	
Stoich.air/fuel ratio(kg/kg)	12,37	

TLC: Thin layer chromatography

AOCS: American Oil Chemist's Society

This specification is a first standardization of MESO as a fuel within the Brazil's program for the utilization of vegetable oils as diesel fuel substitutes (OVEG-1), which is co-ordinated by STI/MIC (Industrial Technology Secretariat/Ministry of Industry and Commerce).

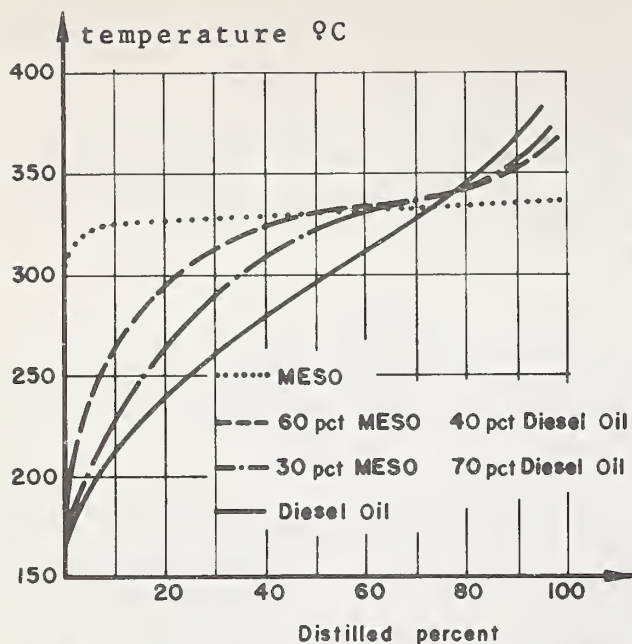


Figure 1. Distillation curves

The diesel oil used in MESO/diesel mixtures came from VW's regular filling stations and was within the Brazilian specifications shown in table 2. Brazilian diesel oil contains low-cetane naphtha and light fuel oil fractions as extenders, which is tolerated by the specification.

Comparison of MESO with diesel oil shows that most of its properties are in line with the requirements of today's diesel engines, however, its distillation curve shows a substantially lower volatility, which is naturally reflected in its mixture with diesel oil, figure 1.

Table 2: Brazilian diesel oil specification

	Specified Value	Method
85 percent distilled volume(°C)	max. 370	ASTM D-86
Calculated cetane index	min. 45	ASTM D-976
Kinem.viscosity at 37.8°C (cSt)	1.6-6.0	ASTM D-445
Carbon residue (wt. %)	max. 0,30	ASTM D-524
Sulfur (wt %)	max. 1.3	ASTM D-129
Ash content(wt. %)	0.02	ASTM D-482
Corrosivness at 50°C	max. 2	ASTM D-130
Water and sediments (% volume)	max. 0.10	ASTM D-1796
Colour	max. 3.0	ASTM D-1500
Cloud point (°C)	max.9-12 (1)	ASTM D-97

(1) Depending on region and season

TESTS AND RESULTS

Straight Methylester of Soybean Oil in Unmodified Engines

Indirect injection engine-- The main results of a comparative dynamometer test on a VW engine, at full load, fuelled alternatively on diesel oil and MESO can be resumed as follows: The delivery of the injection pump is a little higher with the ester (on the average 7 per cent) due to internal hydrodynamic variations in the pump. As the net volumetric calorific value of the MESO is about 6 percent lower than that of diesel oil, this may explain the increase in volumetric specific consumption. Power and torque differ only marginally, but smoke emission is much lower with the methylester.

In Volkswagen's rigorous durability testing, the engine was oper-

ated for about 70 per cent of the 1,400 hours at maximum power and about 20 per cent at maximum torque. Throughout the durability test with straight ester, the same procedures set up for testing on diesel oil have been followed to the letter. After the durability run, the engine was torn down for examination and measurement of wear. Bearings, piston rings, cylinder bores, valve train, and fuel-injection pump remained within VW specifications.

Measured on the chassis dynamometer in the U.S. driving cycles, with a delivery van fueled alternatively on MESO and diesel oil, the fuel consumption falls in the range expected in view of the ester's net volumetric heat content, CO emissions are much lower and NO_x is about the same. A complete description of these tests has already been published (3).

Direct injection engine-- Up to this writing, two 13-ton GVW trucks in day-to-day service with our Transport Department have accumulated 130,000 km on straight MESO. For comparison, we operate two trucks of the same characteristics on diesel oil in the same type of service. Testing is carried out in a joint program with MWM do Brasil, Shell Brasil, VW Caminhões Ltda., and VW do Brasil as participants. This test is still under way. In a comparative consumption test with one diesel oil truck and one MESO truck, consumption was 2 to 4 percent higher with MESO. Drivability and performance were comparable.

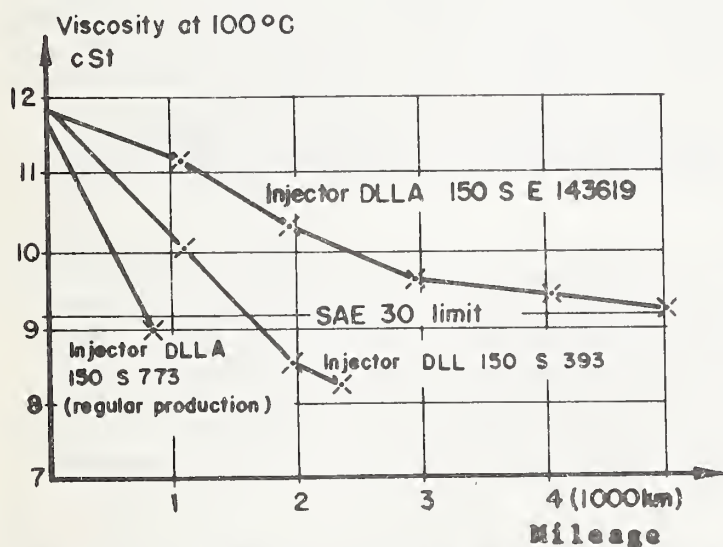


Figure 2. Viscosity drop as function of different-type injector nozzles

At the moment, the only (but undoubtedly critical) problem to arise was that of excessive lubricating-oil dilution by MESO. Figure 2 shows the sharp drop in viscosity of the API CD lube oil over the drain period. We change the lubricating oil when viscosity at 100°C drops below the lower limit of the range specified by the engine manufacturer. This limit is reached at about 20 per cent of the 5,000 km drain period specified for operation on diesel oil. This short drain period, providing little time for chemical reaction, does not permit the interaction between MESO and the lubricating oil.

Ways to Minimize Lubricating-Oil Dilution

The following two solutions to improve the MESO combustion in direct injection engines are being investigated, since a high dilution of the lubricating oil by unburned MESO was observed in the unmodified engine:

Minor engine modifications-- We have only checked those minor modifications that could easily be included during normal servicing. Up to now, the best results in minimizing the lubricating-oil dilution have come from dimensional changes to the injector holes, which directly influence the spray pattern-- and this can be done in the field by simple parts substitution. The drop in viscosity of the API CD lubricating oil over the drain period with two different test injectors is also plotted in figure 2. Even with this new injector, the lubricating-oil dilution by MESO measured by infrared is about 9 percent volume at the end of the drain period. Even with this high dilution, the lube oil maintained a good alkaline reserve and a low quantity of insoluble contaminants. We believe that this lube-oil behavior is closely related to the light work done by the trucks. Other tests under different conditions have still to be carried out.

Mixtures of MESO with diesel oil-- Tests were carried out in order to determine what proportions of MESO could be mixed into the diesel oil without affecting its compatibility with the regular-production VW truck nor shortening the lube-oil change periods recommended for operation on diesel oil. Testing was begun on a VW D-950-S truck running on diesel/MESO mixtures in volumetric proportions of 40/60, 60/40, and 70/30. For the tests with these mixtures, the truck was driven in the same way that, when running on straight MESO, produced a high degree of lubricating-oil dilution by the fuel. The performance of the vehicle running on the mixtures mentioned proved, in all cases, to be similar to that obtained on straight diesel oil, and so was cold starting. This was for ambient temperatures above +10°C.

As the main point of this investigation was the crankcase dilution, major attention was directed to lubricating-oil behavior. Throughout this series of tests with fuel mixtures, the lubricating oil was always SAE 30, API CD from the same manufacturing batch. Samples were taken when the engine had operated for ten minutes on the new charge and thereafter at every 1000 km run. The results of lubricating-oil analyses during the tests, together with comments on them, are given below.

Viscosity: MWM recommend, for this type of engine, an SAE 30 lubricating oil. First attempts, therefore, were directed at determining the highest percentage of MESO in the fuel that would permit using the lubricating oil for the full period specified between oil changes, without its kinematic viscosity at 100°C dropping below the lower limit for an SAE 30 lubricating oil, that is, 9.3 cSt. Increasing the percentage of MESO in the fuel results in a greater

decrease in the lubricating oil's kinematic viscosity at 100°C, figure 3.

The same behavior is seen to occur in the case of the kinematic viscosity at 40°C, figure 4. The lower initial viscosity of the lubricant employed when running the engine on diesel oil is due to the lubricant's having come from a different manufacturing batch, even though it was of the same type as that used for testing with the mixtures.

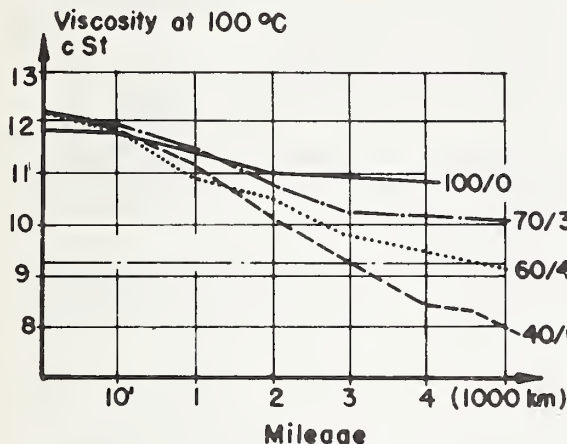


Figure 3. Viscosity drop as function of different diesel/MESO blends.

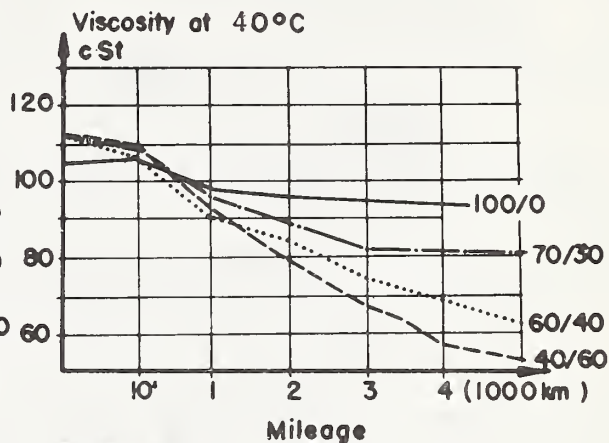


Figure 4. Viscosity drop as function of different diesel/MESO blends.

It was necessary to safeguard the viscosity values from the effect of thickening of the lubricating oil by the oxidation of the MESO contained in it, as this would make it impossible to define the oil-change point as a function of the viscosity. For this reason, the following procedure was adopted:

- Infrared analysis was used to establish the degree of MESO dilution in the lubricant, as a function of mileage, for each mixture tested, figure 5.
- Then the effect of the dilution on the lubricating-oil viscosity was evaluated, figure 6, and it can be seen that the behavior is similar to that obtained in the laboratory when mixing new lubricating oil with MESO. The viscosities of the lubricating oil used in testing with the mixed fuels are, for a given dilution with MESO, seen to be a little lower than that obtained with new lubricating oil, a fact that is probably due to dilution by diesel oil, which was not measured.

This similarity of behavior indicates that, up till the point of the oil change, the thickening of the lubricant usually associated with severe dynamometer testing on straight MESO did not make itself felt. A paper about the influence of lubricant contamination by methylesters of plant oils on oxidation stability and life has already been published (4).

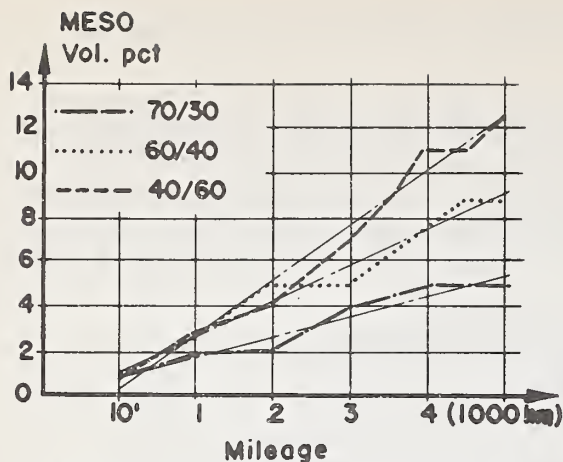


Figure 5. MESO diluted in lubricating oil as function of mileage.

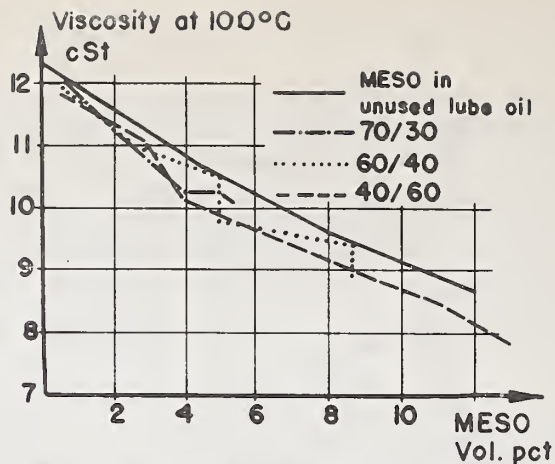


Figure 6. Kinematic viscosity of lubricating oil as function of MESO dilution.

Alkaline reserve/insolubles: the results of the variation of the TBN (Total Base Number) presented in figure 7 show that, in spite of the MESO dilution in the lubricating oil having reached 13 percent volume at 5000 Km on a 40/60 diesel/MESO mixture, the lubricant still has an adequate alkaline reserve. The TBN values in the case of diesel oil are seen to be above those for the mixtures at the end of the drain period, which may have been caused by the new lubricating oil added during the run on this fuel. The insolubles in toluene were found to be at lower levels than those obtained with diesel oil, figure 8. It is interesting to note that the rate of increase of the insolubles in toluene is seen to be proportional to the percentage of diesel oil in the fuel.

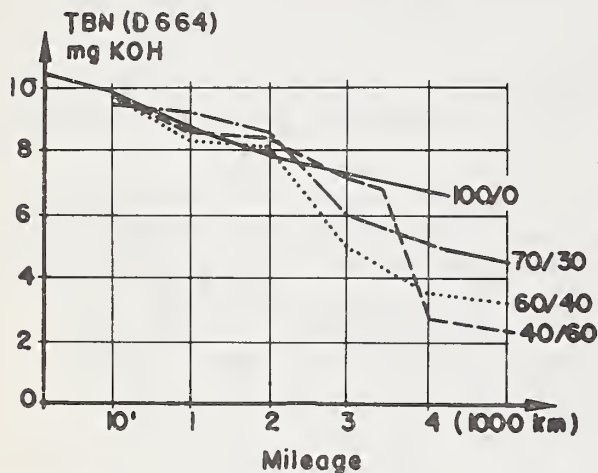


Figure 7. Alkaline reserve as function of mileage.

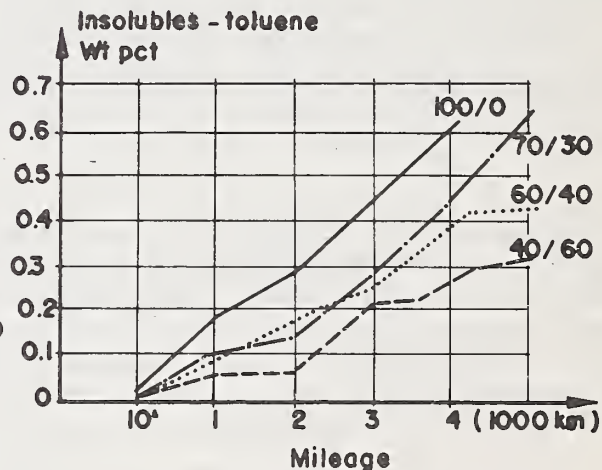


Figure 8. Insolubles in toluene as function of mileage

On the basis of these results, for this type of vehicle utilization, it may be concluded that the percentage of MESO in the fuel, which will permit reaching the oil-change periods recommended for diesel oil, should be little above 30 percent by volume, this figure being adopted, for the present, as the mixture sought.

CONCLUSION

The two types of engine discussed differ totally in behavior when fueled on straight MESO. The swirl-chamber, high-compression IDI engine gave good results, with no abnormal combustion-chamber deposits, due to a relatively complete combustion of the MESO fuel. Thus the lubricating-oil dilution is very low, and the engine can be operated satisfactorily on straight MESO. By contrast, a typical DI engine cannot be operated on straight MESO because of the excessive lubricating-oil dilution.

A first step in avoiding the shortening of oil-change periods because of the premature drop in viscosity resulting from lubricant dilution by MESO could be either the modifying of the injector spray pattern or the limiting of MESO addition to diesel oil to 30 percent in volume. Further investigation is needed into the chemical interaction between the MESO and the lubricating oil under different conditions for the purpose of determining the maximum allowable lubricating-oil dilution by MESO.

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EMISSIONS AND LUBRICATING-OIL PROBLEMS

NONREGULATED EXHAUST EMISSIONS OF VOLKSWAGEN'S IDI ENGINE
FUELED WITH TRANSESTERIFIED OR REFINED SOYBEAN OIL EITHER
STRAIGHT OR BLENDED INTO GASOIL

R. W. Siekmann, G. H. Pischinger, and H. Joseph, Jr. ^{1/}

ABSTRACT

It was suspected that the incomplete combustion of glycerol contained in plant oils, resulting in acrolein, could contribute to the formation of combustion chamber deposits. A Volkswagen 1.6 liter IDI engine was fueled both with blends of gasoil with refined soybean oil and ethylester of soybean oil (EESO) and with EESO as a straight fuel. The relative amounts of acrolein are measured and discussed.

INTRODUCTION

From DI engine tests, it is reported that the use of refined unmodified plant oil, both as straight fuel or in gasoil blends, results in serious combustion chamber deposits and injector nozzle coking (1, 2, 3, 4). These problems can be eliminated by the transesterification of the plant oils, giving products with fuel-relevant characteristics that satisfactorily meet the current diesel fuel requirements (5, 6). As the transesterification process eliminates the glycerol of the plant oil by substitution with low-molecular-weight alcohols, it was suspected that the incomplete combustion of the glycerol, resulting in acrolein, could contribute to the formation of deposits in the combustion chamber. In order to evaluate the relative amounts of acrolein formed during the combustion process, we analyzed the exhaust emission of our Volkswagen 1.6 liter IDI engine, installed in a light-duty delivery van. The same vehicle was fueled both with blends of gasoil with refined soybean oil and EESO and EESO as a straight fuel.

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TEST PROCEDURE

Test Vehicle and Fuels

The test vehicle is characterized as follows:

Vehicle:

type	: pick-up
type of use	: light-duty delivery van
pay load	: 1075 kg
total load	: 2265 kg

Engine:

cylinders	: 4 in line
injection	: indirect, swirl chamber
displacement	: 1588 cm ³
compression ratio	: 23
injection pump	: rotary

The utilization of this type of vehicle is advantageous as it offers the possibility of testing on the chassis dynamometer and because of the great tolerance of the IDI engine to various fuels.

The following straight fuels and mixtures were tested:

- 100 percent gasoil
- 70 percent gasoil + 30 percent soybean oil
- 70 percent gasoil + 30 percent EESO
- 50 percent gasoil + 50 percent soybean-oil
- 50 percent gasoil + 50 percent EESO
- 100 percent EESO

Determination of Acrolein

We used the DNPH method for the determination of acrolein, which is based on the reaction of aldehydes and ketones contained in the exhaust gas with an acidified aqueous solution of 2,4 dinitrophenylhydrazine (DNPH). An insoluble derivative is formed, corresponding to each carbonyl function, which can subsequently be identified and quantified by gaschromatography.

Sampling of the exhaust gas was carried out, running the EPA-74 cycle with warm start. The undiluted gas sample was taken by a probe tube, which was introduced into the exhaust pipe, and by means of an auxiliary pump bubbled through a pair of impingers containing the reagent. The gas flow was adjusted to 1.0 l/min. The gas sample volume was simultaneously measured and corrected to normal conditions. The sampling procedure was carried out during the 1372 seconds of cycle duration.

After the sampling, we extracted the aqueous solution containing the DNPH-derivatives with n-pentane.

After evaporation of the solvent, the extract was quantitatively dissolved in toluene containing anthracene as internal standard. An aliquote amount of 1 μ l was then injected into the gaschromatograph. The apparatus was equipped with a flame ionization detector (FID), high speed capillary column of 12,5 m length, 0,2 mm i. d.

The column phase was crosslinked dimethyl silicone, deactivated with siloxane. The temperature was programmed at between 190 and 230°C.

The method identifies the derivatives of the following compounds: formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, methyl ethyl ketone, n-butylaldehyde, crotonaldehyde, n-valeraldehyde, and benzaldehyde. These compounds were also used as standards to calibrate the gaschromatograph.

The concentration of the DNPH-derivatives encountered was correlated to the molecular weight of the carbonyl compounds and the gas sample volume, thus obtaining the concentration of the various aldehydes and ketones.

RESULTS

The concentrations of acrolein encountered are shown in figure 1, taking the exhaust value of straight gasoil operation as 100 percent.

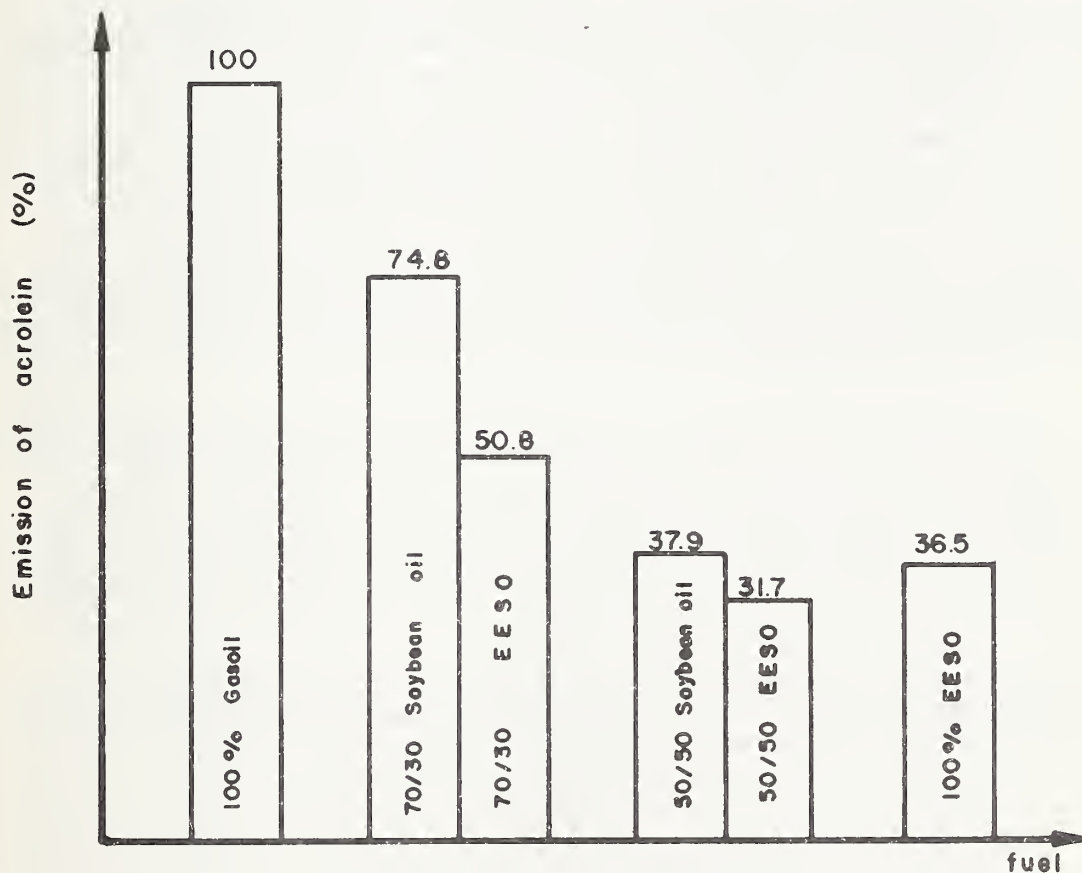


Figure 1.-- Relative acrolein emission.

It can be observed that for this type of engine and test method, an increasing substitution of gasoil results in reduced acrolein emissions. As mentioned initially, the transesterification in fact contributes to lower emissions, the difference being quite significant in the case of the 70/30 blend.

However, there are other influences on the combustion process and the resulting emissions as, for instance, the different viscosities of the fuels tested, which certainly produce variations in the spray characteristics.

As can be seen from fig. 1, the highest emissions of acrolein occur in operation on straight gasoil, but this does not result in excessive carbon deposits. Consequently it would seem that the acrolein production is not the main reason for the greater deposits from DI operation on unprocessed plant-oil.

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SINGLE-CYLINDER DIESEL ENGINE STUDY OF RAW AND TRANSESTERIFIED VEGETABLE OILS

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ABSTRACT

A single cylinder, 0.36 L, D.I., Avco-Bernard diesel engine was operated on No. 2 diesel fuel, sunflowerseed oil (SSO), cottonseed oil (CSO), methylester sunflowerseed oil (MSSO), and methylester cottonseed oil (MCSO). The objective of this study was to obtain a detailed comparison of engine performance and emission data when operating on raw vegetable oils, transesterified vegetable oils, and diesel fuel.

Results comparing the various fuels generally show slight improvements in brake thermal efficiency and shorter ignition delays when operating on vegetable oils, higher NO_2/NO_x ratios with vegetable oils, and higher total aldehydes and lower indicated specific revertant emissions with vegetable oils.

INTRODUCTION

In order to have a decreased dependence on foreign oil, domestic alternative sources of motor fuel must be developed, especially renewable sources. Vegetable oils are of particular interest in the agriculture sector for use in diesel engines, primarily as emergency fuels.

Raw vegetable oils cause numerous engine related problems (1,2)^{2/} because of their high viscosity, which leads to poor atomization and incomplete combustion. Further, the presence of triglycerides can cause varnish to build up on the cylinder walls and the injector tip when operating on vegetable oils (3). Raw vegetable oils can be modified by the process of transesterification, which removes the triglycerides and replaces them with radicals from the alcohol used for the conversion process (4). The transesterified vegetable oils have lower viscosities and improved cetane numbers.

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^{2/}Numbers in parentheses refer to references at the end of the paper.

The primary objectives of this study were to assess the potential health effects of particulate emissions, since they are suspected to be harmful to biological systems (5,6), and to assess the aldehyde emissions, since they are believed or suspected to cause severe eye and nose irritation, to participate in photochemical smog reactions, and to contribute to objectionable odor (7). A partial review of prior aldehyde work on diesel engines may be found elsewhere (8).

DESCRIPTION AND RESULTS

A single-cylinder, direct-injected diesel engine (Avco-Bernard W-51, 0.36 L) was operated at 2400 RPM and load conditions of 1.12 bkW at 1/3 rack, 2.24 bkW at 2/3 rack, and 3.00 bkW at full rack. The fuels tested were two vegetable oils, their methylesters, and a certified number two diesel fuel (DF-2). The objectives were to obtain performance data; obtain gas-phase emission data for CO, HC, NO_x, and total aldehydes; and collect exhaust particulate matter to document the biological activity of the soluble organics extracted from these solid-phase emissions. The vegetable oils were then compared to the DF-2 baseline.

The diesel engine was fully instrumented to provide performance information. Complete details of the instrumentation, gas-phase equipment, and aldehyde procedures used in this study are available elsewhere (8,9,10).

Figure 1 shows the brake thermal efficiency (BTHEFF) and ignition delay (IGNDLY) data. For clarity, the vegetable oil values are presented as averages and ranges. The BTHEFF for the raw vegetable oils was slightly improved when compared to the DF-2 baseline. The BTHEFF for the methylester vegetable oils was approximately equal to the DF-2 baseline. The IGNDLY for the raw vegetable oils and their methylesters was generally shorter when compared to the DF-2 baseline. The reduced viscosity and improved spray characteristics resulting from the esterification process are the probable cause for the shorter IGNDLY for the esterified vegetable oils at 1/3 rack and 2/3 rack when compared to the raw vegetable oils. However, at full rack, the shorter IGNDLY observed for the raw oils is probably caused by increased combustion temperatures resulting in better atomization of the raw oils; the esterified oils are probably limited in their combustion characteristics by the radicals that are added during the esterification process, causing very little change in the IGNDLY of the esterified oils from 2/3 to full rack.

Figure 2 shows the oxides of nitrogen (NO_x and NO₂/NO_x) data. The NO_x and NO₂/NO_x for the raw vegetable oils and their methylesters are generally higher when compared to the DF-2 baseline. The structure and the increased availability of monatomic oxygen of the vegetable oils and their methylesters are the probable cause for this observation.

Figure 3 shows the indicated specific total aldehyde emissions (ISTA) and the indicated specific revertant emissions (ISRE) data. Ames Test values for the ISRE were taken as the slope of the linear portion of the dose response curve using TA 98⁻ bacteria. The ISTA for the raw vegetable oils and their methylesters are significantly higher than DF-2, probably because of the oxygen contained in the vegetable oils. The ISRE for the raw vegetable

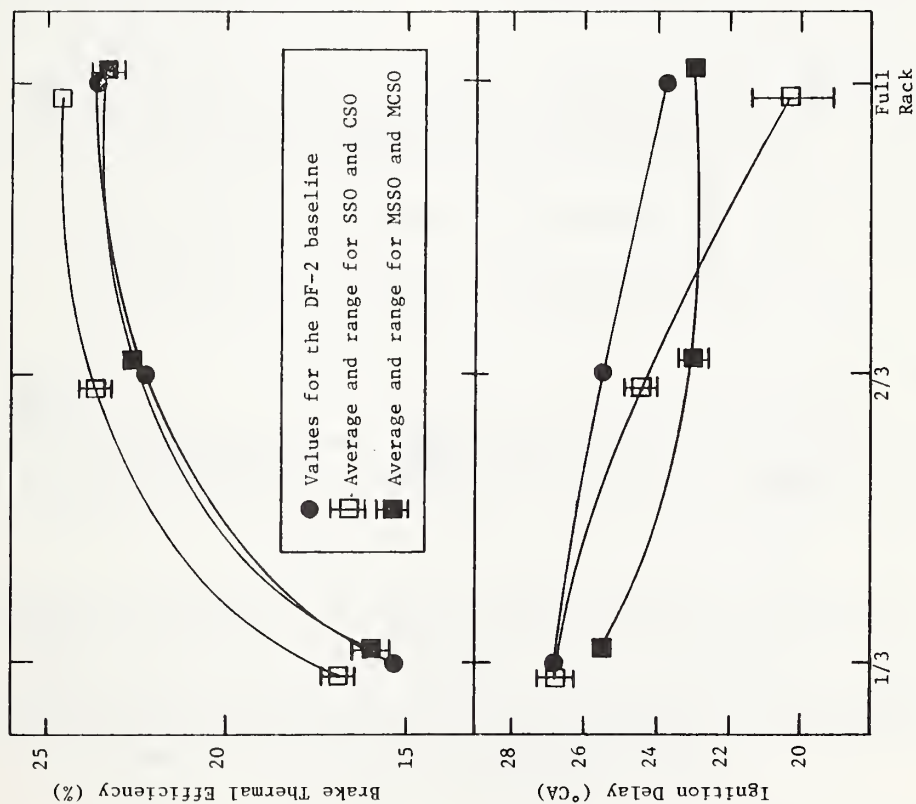


Figure 1 - Brake Thermal Efficiency and Ignition Delay as a Function of Rack at 2400 RPM.

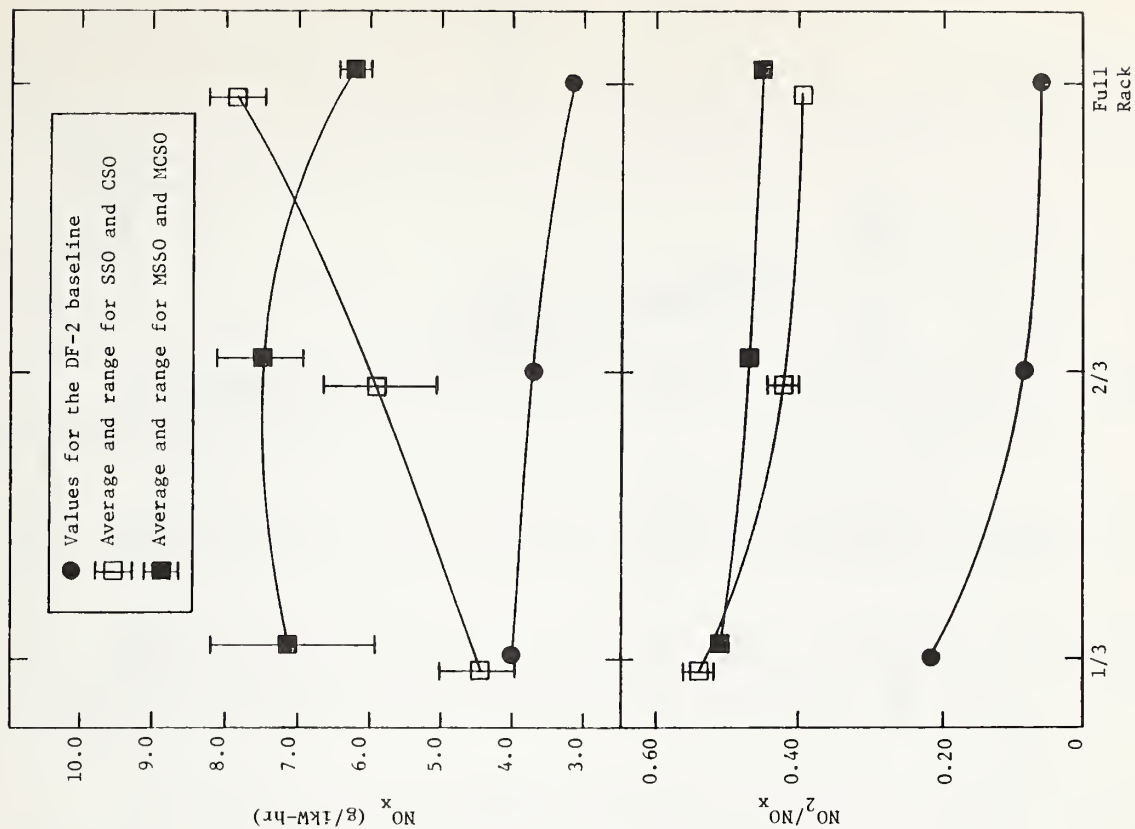


Figure 2 - NO_x and NO_2/NO_x as a Function of Rack at 2400 RPM.

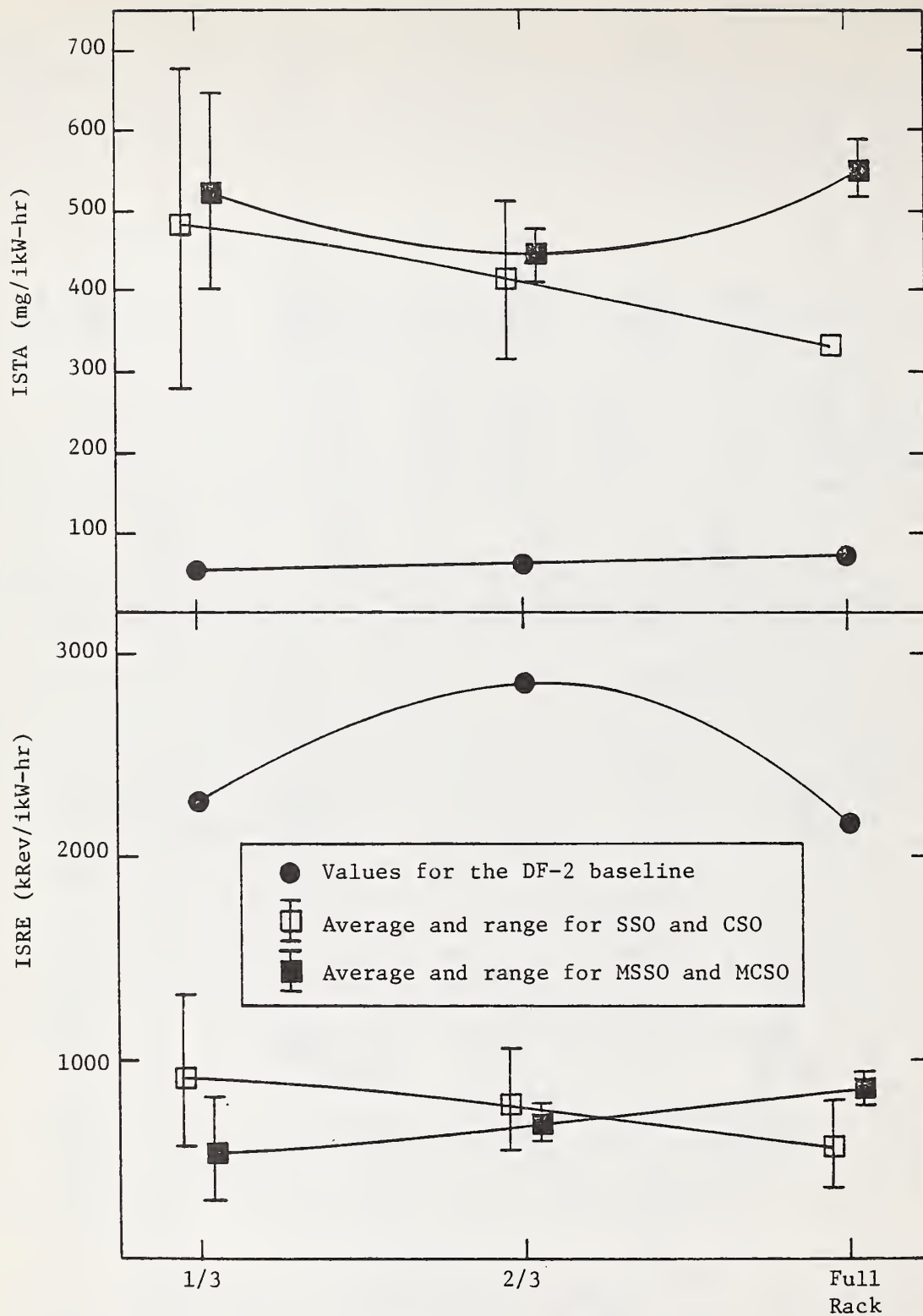


Figure 3 - Indicated Specific Total Aldehydes and Indicated Specific Revertant Emissions as a Function of Rack at 2400 RPM.

oils and their methylesters are significantly lower than the DF-2 baseline, influenced primarily by the lower Ames Test values of the vegetable oils. It is interesting to note that the ISRE for the vegetable oils were significantly lower than for DF-2 while the ISTA were significantly higher for the vegetable oils than for DF-2.

CONCLUSIONS

The following conclusions may be drawn from this study:

1. Brake thermal efficiency was improved slightly with the use of raw oils and was approximately equal with the use of the methylesters when compared to the baseline DF-2.

2. Ignition delays were generally shorter with the use of vegetable oils when compared to DF-2. The raw oils showed more pronounced decreases in ignition delay with increasing load than did the esterified oils or DF-2.

3. The oxides of nitrogen were higher with the vegetable oils than with DF-2 at all conditions except the raw oils at 1/3 rack; the NO_2/NO_x ratio was very consistent and was significantly higher for the vegetable oils when compared to DF-2.

4. The indicated specific total aldehyde emissions were significantly higher for the vegetable oils when compared to DF-2; the average of the esterified oils was higher at all rack settings than the average of the raw oils, particularly at full rack.

5. The indicated specific revertant emissions were significantly lower with the vegetable oils when compared to DF-2; no significant differences between the raw oils and the transesterified oils were noted.

ACKNOWLEDGEMENT

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EVALUATION OF LUBRICATING OIL CONTAMINATED WITH SMALL
AMOUNTS OF SOYBEAN OIL ESTER IN COMPARISON WITH NORMAL
DIESEL OIL OPERATION

R. W. Siekmann and G. H. Pischinger^{1/}

ABSTRACT

DI engine operation with esters of plant oil as straight fuel results under certain conditions in an excessive lubricating-oil dilution that may influence the lubricating capacity.

In order to evaluate this occurrence, samples of various lube-oil/ester mixtures are tested in the Four Ball Tester. While new lube oil (MIL-L 2104C, API CD, SAE 30) contaminated with up to 35% of ethylester of soybean oil showed reduced wear properties, used lube oil containing 5% of ester demonstrated greater wear.

INTRODUCTION

Plant oils, particularly in the form of their methyl- and ethylesters, show a high potential for gasoil substitution. The transesterification modifies most of the fuel-relevant properties of plant oil so that they meet the most important diesel requirements, specially adequate viscosities and cetane numbers(1).

Engines fueled with methylesters showed that combustion chamber deposits, observed when using unprocessed plant oils, were practically eliminated. Tests with the Volkswagen 1.6 liter IDI engine gave totally satisfactory results (2). DI engine operation with esters of plant oils, however, results under certain conditions in high-lubricating oil dilution with the consequence of unacceptable low viscosities (3, 4).

Modifying the design of injector nozzles or the use of gasoil/ester blends can reduce lubricating-oil dilution to acceptable viscosities (5). While laboratory and vehicle tests indicate that small dilution rates of ester can be handled by the lube oil without consequences to oxidation stability and life (6, 7), little is known about their influence on the lubricating capacity of the oil.

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The present work aims to evaluate, in a preliminary laboratory test, the lubricating behavior of oil contaminated with different amounts of soybean ester as compared with that of normal lube oil.

TEST PROCEDURE

Lubricating Oil Samples

In Brazil, due to the availability of biomass-based ethanol, ethylesters of plant oil will most probably play a more important role than methylesters. Since the beginning of 1983, a government-supported fleet test has been under way that uses ethylester of soybean oil (EESO) in a 30 percent blend with gasoil.

This is why we conducted lubricating tests with EESO, analyzing various amounts in the range of 1 to 35 percent blended into unused lubricating oil of specification MIL-L-2104 C, API CD, SAE 30. The lower viscosity limit for engine operation corresponds, for this oil, to an ester dilution of about 9 percent.

Normal Diesel engine operation with gasoil generally causes only low lube-oil dilution rates. The resulting decrease in viscosities is thereby highly overcompensated by oilthickening due to the formation of oxidation products and increasing soot content.

In order to compare the test results with those for normal gasoil operation, lubricating-oil dilution by gasoil was also simulated but limited to a realistic value of 5 percent. As it may be assumed that it is mainly the unburnt heavier parts of the gasoil that are causing lube-oil dilution, we removed, by distillation, lighter fraction totalling 50 percent by volume of the gasoil. Blends of 3 and 5 percent of this heavy gasoil fraction (D_h) were prepared and analyzed. For comparison, the same procedure was carried out with normal gasoil (D_n).

In complementation, we determined the wear characteristics of a used lube oil of the same specification, drained after 9126 km of normal DI-engine operation under mixed driving conditions with gasoil as fuel. That same used oil sample was contaminated with 5 percent of EESO and D_n , respectively, and subsequently submitted to the testing procedure. Test materials and mixtures examined are compiled in table 1 and characterized with respect to viscosity, density, and water content.

Test Apparatus and Procedure

For a first evaluation of the lubricating characteristics of the samples, the conventional Shell Four Ball apparatus was used. The Four Ball Tester was developed to determine the extreme pressure, anti-wear and anti-weld properties of lubricants.

This machine measures both normal friction and wear at loads below those at which seizure occurs and also the onset of seizure and its intensity.

As the preliminary tests run at a load of 150 N showed only little differences in wear, all tests were carried out for one hour at a load of 375 N and a speed of 1420 rpm.

After the test run, the wear characteristics of the lube-oil samples were evaluated by measuring the scar diameters both parallel and normal to the striations in the scar surface of the three test balls. All test runs showed good agreement in the scar diameters of the three balls, and repeatability in two tests was found to be highly satisfactory.

Table 1.--Samples submitted to Four Ball Test

Sample	Kinematic viscosity cSt 37.8°C	98.9°C	Density 20/42	Water content percent
new lube oil, lot A	128.84	12.8	0.898	0.03
lube oil A + 3 percent EESO	110.9	11.6	0.897	0.05
lube oil A + 5 percent EESO	96.7	10.9	0.896	n. d.
lube oil A + 10 percent EESO	75.9	9.5	0.895	n. d.
lube oil A + 3 percent D _n	113.7	11.9	0.895	0.03
lube oil A + 5 percent D _n	104.2	11.3	0.895	n. d.
lube oil A + 5 percent D _n	96.0	10.5	0.893	0.04
heavy gasoil D _h	5.4	1.7	0.863	n. d.
used lube oil	140.5	13.1	0.902	0.04
EESO	4.9	1.9	0.878	0.12

TEST RESULTS

Lube-Oil/EESO Blends

In a series of tests, the influence of ethylester of soybean oil added to the unused lube oil was determined and correlated with normal lube oil wear measurement. The results are showing in figure 1.

Starting with an average scar diameter of 0.414 mm, as determined for the pure lube oil, an addition of ethylester results in obviously reduced wear diameters, with the minimum value found at about 3 percent dilution. The evaluation of mixtures with higher dilution rates demonstrated increasing wear rates, reaching at about 38-percent dilution the initial value of the pure lube oil.

The pure ester evaluation tests produced the significantly high value of 1.009 mm mean scar diameter.

As we assumed that the initial reduction in wear at low dilution rates could reflect an interaction of the ester with the small amount of water detected in the lube oil, the test procedure was repeated with another lot of the same oil but containing only traces of water as identified by infrared spectros-

copy. In general, the same effect of reduced scar diameters was observed, although less pronounced.

In comparison with the lube-oil/ester blends, testing of lube oil contaminated with 3 and 5 percent of the heavy diesel fraction showed more intense wear characteristics, although they remained below the initial value for pure lube oil (see figure 2). The reference test carried out with 5 percent of normal gasoil D_n showed no significant difference in wear behavior.

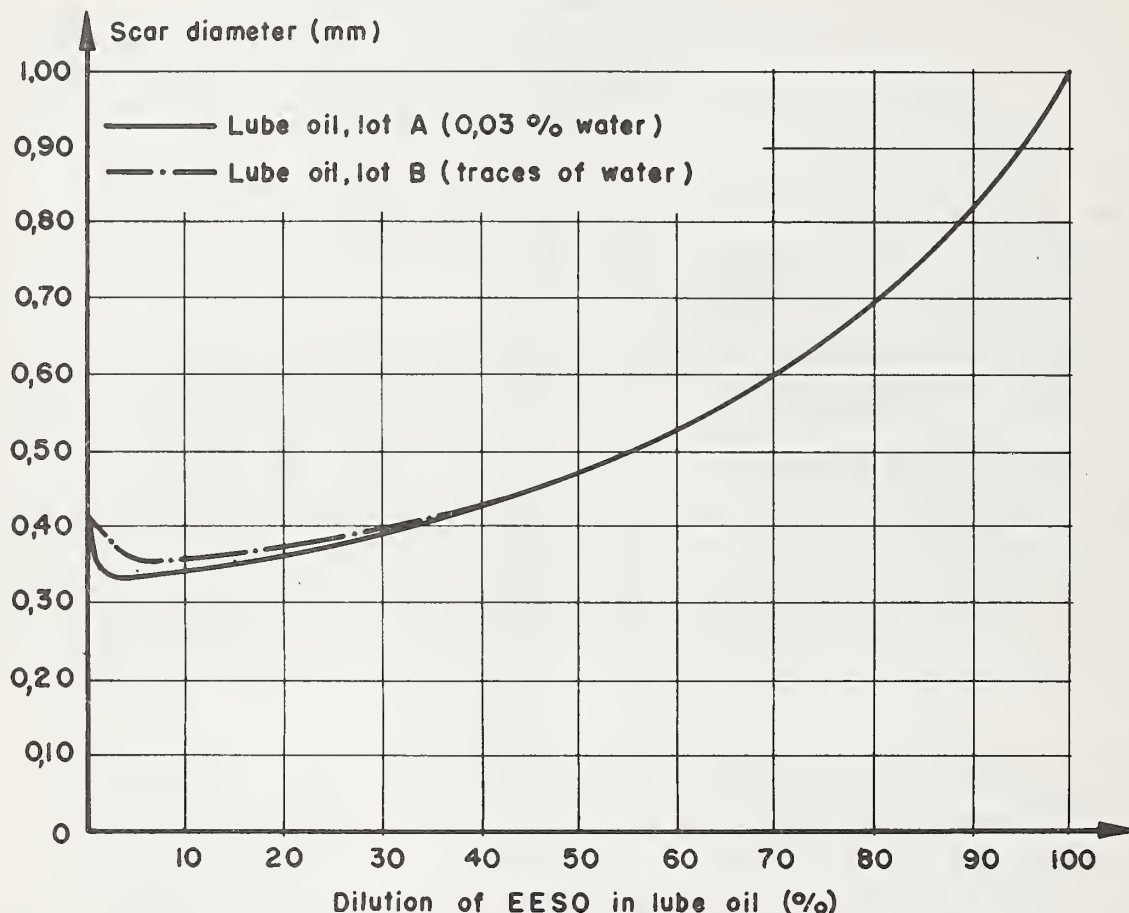


Figure 1. Wear as function of EESO contamination.

It should be taken into account that distilling off the initial 50 percent of the gasoil might not quite simulate the real occurrence of unburnt fuel in the lubricating oil and serves only as an indication. More significant results could probably be obtained by testing with lubricating oil used in engine operation and then contaminated by EESO and gasoil, respectively. The results shown in figure 3 demonstrate the altered characteristics of the used oil.

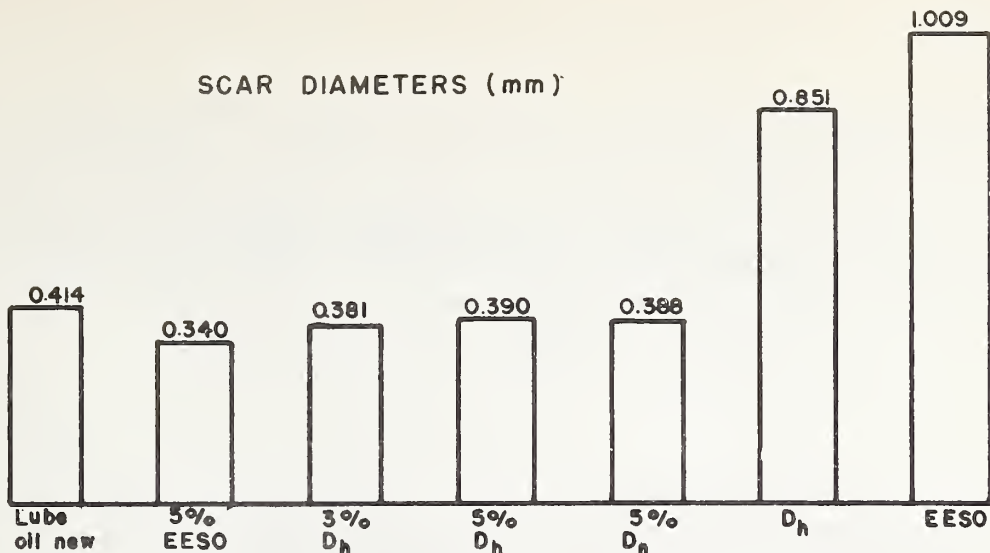


Figure 2.--Wear measurement of Lube-oil/ester and -/gasoil blends.

It should be noted that the sample is of the same specification and make but from a different lot than the new lube oil tested. The used oil, which already has reduced anti-wear potential due to partial degradation of the additives, shows a quite different behavior when contaminated with EESO or the heavy gasoil fraction. Contaminating the used oil sample with 5 percent EESO results in an increase in mean scar diameter, an effect that is not observed when adding 5 percent of the heavy gasoil fraction. In order to confirm this behavior, we added 5 percent of EESO to the sample already contaminated by 5 percent of heavy gasoil and then submitted it to the test procedure. The addition caused an increase in mean wear diameter from 0.478 mm to 0.544 mm, which is only slightly higher than expected and practically confirms the influence of the ester contamination.

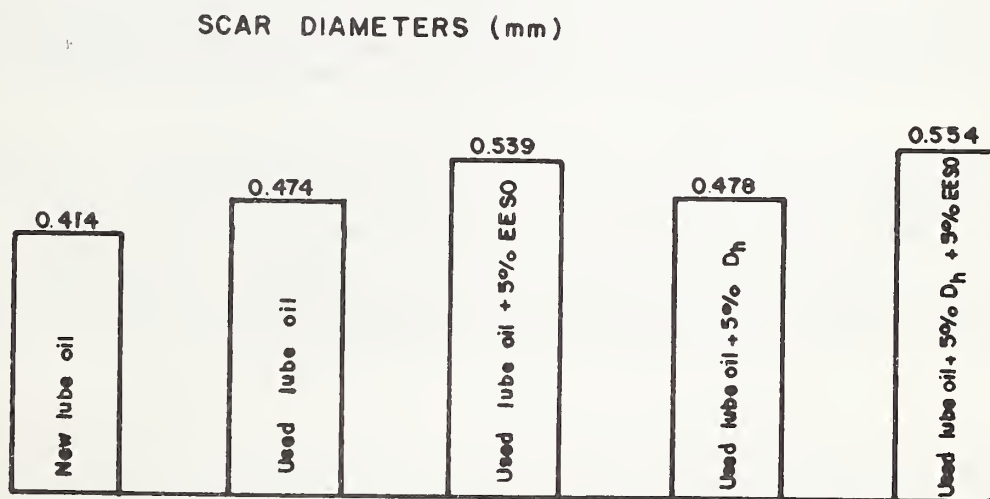


Figure 3.--Wear measurement of used lube-oil/ester and -/gasoil blends

CONCLUSIONS

Our preliminary results, obtained in the Shell Four Ball Tester, showed that new lube oil contaminated with up to about 35 percent of ethylester of soybean oil had better wear-resistant qualities. In contrast, used lube oil containing 5 percent of EESO demonstrated greater wear than a similar sample containing gasoil. More information, however, is needed before coming to a final conclusion, including also test procedures that simulate other types of lubrication, like, for instance, the cam-tappet test.

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PERFORMANCE OF LUBRICATING OILS IN VEGETABLE OIL/ESTER FUELED DIESEL ENGINES

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INTRODUCTION

Strong interest continues in some countries to prove vegetable oils or derivatives as fuels for diesel engines. Literature reports have indicated that 100 pct vegetable oil fuels can give serious problems of combustion chamber fouling, hence attention has turned, for example, to blends of vegetable oils with diesel fuel and to transesterified vegetable oils. Initial engine testing demonstrated 100 pct soya ester to be satisfactory as fuel, although problems were detected as regards injector deposits and the useful life of the lubricant. This latter aspect of fuels and lubricants evaluation has now received more detailed attention.

EXPERIMENTAL

A series of engine dynamometer tests were performed using 100 pct ethyl ester of soya oil as fuel and six diesel engine lubricants covering a wide range of performance specifications and additive composition. In each case the lubricant became contaminated by unburnt fuel during the test (0.2 pct of total fuel throughput). The lubricant/fuel mixture eventually underwent degradation to such a degree that the tests had to be interrupted to avoid engine damage because of inadequate lubrication.

DISCUSSION

Detailed analysis revealed that rapid oxidative polymerization of some of the fatty acid components of the fuel had occurred in the later stages of the tests. The products of this complex reaction were poorly soluble in the lubricant and eventually phase separation occurred.

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The severity of this problem was shown to depend on several factors: engine construction, service conditions, fuel chemistry, and type of lubricant additives. Very heavy rates of contamination of the lubricant, such as in city-cycle driving, resulted in excessive dilution to the point that the oil became too thin for continued use before oxidation occurred.

The rate of dilution of the crankcase oil by ester was influenced by the presence of other components in the fuel, notably automotive gas oil or ethanol. Admixture of soya ester with diesel fuel or ethanol resulted in a much lower dilution rate, i.e., more complete combustion than might have been expected from a simple fuel composition ratio basis. Thus one way of extending lubricant life with vegetable oil fuels would be to utilize vegetable oils or esters as extenders rather than substitutes for conventional diesel fuel. Furthermore, fuel extension appears to be more in line with the likely availability of vegetable oils for fuels use, and the indications are that these mixtures should be compatible with the existing diesel engine fleet.

SEMINAR REFLECTIONS AND FUTURE RESEARCH NEEDS

M. O. Bagby¹

ABSTRACT

Seminar III presentations are summarized with brief comments. And, I have attempted to identify areas of further consideration for future research. Since 1980, much new knowledge has become available; however, the need for considerable basic information still exists.

INTRODUCTION

Researchers from many countries have recognized the need to identify and develop alternative sources of liquid fuels for farm, construction, and transportation vehicles. Vegetable oils were used as fuels at the turn of the century and later during periods of fuel shortages to power diesel engines. With their low oxygen contents, vegetable oils have about 90 percent of the heat content of diesel fuel. Consequently, they were a natural to be reevaluated when the 1973 petroleum embargo forced the fuel shortages of 1973-1974. The modern high-speed diesel engine performed well on vegetable oils from seeds such as soybean, sunflower, peanut, and coconut; however, endurance tests with diesel engines, especially direct-injection models, burning vegetable oil fuels revealed several problems suggesting inefficient combustion. Because most production-agriculture farm tractors are diesel powered, the U. S. Department of Agriculture (USDA) has a special interest in developing the technology to assure the availability of alternative fuels that will allow crop production to proceed in fuel emergency situations. The USDA, Northern Agricultural Energy Center (NAEC), established in 1980 (Bagby 1981), initiated a vegetable oil as diesel fuel research program; and in the fall of 1980, NAEC sponsored its first seminar on vegetable oil as diesel fuel. That, and the subsequent Seminar II, brought many of the research leaders together. These gatherings facilitated understanding of the research problems and provided better focus for their solution.

This proceedings, which summarize the formal presentations of Seminar III, clearly illustrate that considerable new knowledge has accrued. However, equally obvious, much work remains before a suitable technology will evolve from our knowledge of vegetable oil as diesel fuel.

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DISCUSSION

Fuel Source - Biomass

When alternative fuels for diesel farm tractors are mentioned, the most frequent examples envisioned are seed oils from soybean, sunflower, cottonseed, peanut, rape, corn, palm, etc. However, the opening session of Seminar III was devoted to discussions of liquid fuels potentially available from lignocellulosic plant biomass. Chang² opened the session with an interesting discussion of petroleum evolution and illustrated the role of fatty acids and sugars as carbon sources for catalytic formation of petrochemicals. One example, that of converting sugars via aqueous ethanol to hydrocarbon, was recently reported (de Boks, et al., 1982). Soltes discussed pyrolysis of biomass to tars that were subsequently converted, catalytically, to liquid hydrocarbons. These products can be resolved into fractions that were similar to petroleum distillates. Remarkably similar chemical products were obtained starting with a variety of lignocellulosic waste materials. Kuester described production of diesel fuel from biomass by gasification and catalytic liquefaction. At least 86 feedstocks have been screened. All produced quality, although somewhat diverse, hydrocarbon distillates. Hammaker summarized a study conducted for the Montana Department of Natural Resources and Conservation. Selected mainly from the literature, species (native or adaptable to Montana) were evaluated for potential as oilseed or whole-plant oil-bearing crops. Little or no engine testing has been conducted with any of these biomass resources.

Fuel Sources - Seed Oils

Some uncultivated plant species were discussed by Icerman, Shultz, and Scheld as possible seed oil sources for diesel fuel. The first was buffalo gourd (Cucurbita foetidissima) reported to produce seed (0.5 ton/acre) containing 30-40 percent oil. Because of their high starch content, roots are proposed as substrate for alcohol fermentation. Unfortunately, the arid regions suggested for its production probably will not tolerate the disturbance necessary for root harvest. A short performance test with buffalo gourd seed oil in diesel engine was reported. Shultz and Scheld discussed some observations with Chinese tallow tree (Sapium sebiferum). The seed coat fat is a low iodine value (IV) triglyceride (m.p. 38°C), and the kernal oil is a rather high IV mixture, consisting of triglyceride and estolide. The kernal oil should have good film-forming properties and be undesirable as a fuel. Dykstra reviewed literature of thermal and catalytic decomposition of vegetable oils to hydrocarbons.

²For convenience, the name of the first author and presumably the speaker is cited by my remarks; however, please refer to the contents and the individual paper for complete authorship.

Economics

Johnson discussed the economics of a diverted acreage program to produce fuel from sunflower seed oil. He concluded that a subsidized sunflower production for fuel would probably be more successful in high-yield areas, such as the Corn Belt. Withers examined the economic feasibility of producing oilseed crops in Idaho for on-farm processing to fuel. At current price, he concluded that the production penalty would be about \$0.60/liter.

Processing and Storage

Du Plessis studied oxidative stability of methyl and ethyl esters of sunflower oil and concluded that, compared with ethyl esters, methyl esters exhibit a longer induction time. Induction period was extended by presence of tocopherol or other antioxidants. Al-Kahtani discussed the effect of various quantities of $\text{CaCO}_3\text{-MgCO}_3$, FeCl_2 , and NaCl on degumming and subsequent oxidative stability of soybean oil. FeCl_2 and NaCl at appropriate levels have a beneficial effect on phosphorus removal; however, $\text{CaCO}_3\text{-MgCO}_3$ significantly suppressed degumming. High residual concentrations of the representative salts adversely affected oxidative stability.

Fuel Modification

Engler, Hassett, and Nye discussed their experiences with transesterification of sunflower oil and, the last, rapeseed oil. Engler found that the reaction of ethanol with sodium ethoxide catalyst is very sensitive to moisture and free acid. Hassett prepared methyl esters. They performed about equal to no. 2 diesel fuel; however, they present a cool weather problem. Crystals of methyl ester began to form at about 45°F. Nye suggested that sodium hydroxide catalyzed formation of methyl and ethyl esters could be performed on-farm. Webster discussed a commercial methyl ester based fuel extender. Schwab described microemulsion fuels with viscosities near the upper specification limit for no. 2 diesel fuel. Pryde reviewed engine test results obtained with the EMA 200-hour screening procedure.

Fuel Properties

Ryan developed a preliminary specification for vegetable oil fuels for diesel engines. The specification is based on data and observations derived by examining four vegetable oils at three stages of refining, evaluating their physical and chemical properties, injection and atomization characteristics, and performance and combustion characteristics in both a direct injection (DI) and indirect injection (IDI) engine. Klopfenstein reported that chain-length of methyl esters influences fuel efficiency (maximum methyl decanoate). Unsaturated 18-C esters burn more efficiently than methyl stearate. Cetane rating appears to increase with molecular weight of the acid group and alcohol group; however, the observation is based on a limited group of samples. Unsaturation appears to lower the cetane rating.

EMA Screening Tests

Four research groups discussed results with a variety of vegetable oil fuels screened by the 200-hour EMA-Screening test. Engines of several manufacturers were also used. Ziejewski concluded that a 25:75 blend of high oleic safflower oil with diesel fuel and methyl esters of sunflower oil are promising as fuels for the DI engine. Using an IDI engine, Goodrum observed a 5-percent power loss after 130 hours with 20:80 peanut oil/diesel fuel and after 50 hours with 80:20 blend. Clark found that methyl, ethyl, and butyl esters of soybean oil compared well with no. 2 diesel fuel in a DI engine. However, emissions tests showed that nitrous oxide levels were higher for the esters fuels. Goering evaluated two hybrid fuels in a DI engine. Both fuels pass; however, the microemulsion fuel consisting of 50:25:5:20 (diesel fuel:degummed alkali refined soybean oil:190 proof ethanol:butanol) was a marginal pass because performance had degraded to approximately 5 percent at the end of the 200 hours.

Engine Test - Miscellaneous

Using throttle to misfire technique, Johnson evaluated 27 fuels in both DI and IDI engines. Self-consistent data were obtained with oils and esters. Cetane rating declined as iodine value increased. Quick evaluated linseed oil with a 1000-hour engine test. Strayer tested canola oil, methyl ester, and rapeseed oil and reported discouraging results. Pischinger reported that soybean oil methyl esters performed well in a DI 13-ton truck; however, crankcase dilution by unburned fuel was excessive.

Emissions and Lubricating-Oil Problems

Siekmann reported that acrolein in emissions is greater from diesel fuel than from soybean oil or ethyl esters. Geyer compared diesel fuel and vegetable oil and found that the latter had better brake thermal efficiency and shorter ignition delays, higher NO_2/NO_x ratio, and higher aldehyde emissions. Siekmann found that fresh lubricating oil contaminated with up to 35 percent ethyl ester of soybean oil caused reduced wear; however, even 5 percent ester in used lube oil resulted in increased wear. Blackburn reported that soybean-ester diesel fuel solutions burn more completely than might be expected from a simple fuel composition ratio.

CONCLUSIONS AND RECOMMENDATIONS

The several, more novel, potential liquid fuel sources offer considerable technical potential; however, they are unlikely to serve as emergency fuels in the near term. Each requires considerable long term research to evolve into a new technology. Undoubtedly, all would initially need a higher value market for their principal product. Further technological developments including performance evaluations are necessary, as well as, determining economics and conducting marketing research. Besides the above, underutilized species considered for new crops also require research to establish cultural practices, harvesting and handling procedures, processing, and storage techniques. The chemistry of the Chinese tallow lipids probably

preclude their use as fuels; however, their unique characteristics may dictate other higher value uses. Buffalo gourd may provide significant above-ground produce; however, production of the gourd on arid lands may preclude the harvest of roots from such a fragile ecosystem.

Transesterification is a promising approach for modifying seed oils to provide lower viscosity fuels. The reaction kinetics need further delineation, and the limits of ester purity need to be established. The economics for ester processing and storage, including scale of plant size, should be determined.

Microemulsion fuels offer considerable potential for improved atomization of fuels containing appreciable seed oil. More basic information should be obtained to better understand the physical-chemical parameters of microemulsions, and additional formulations should be evaluated.

Several researchers have recommended engine modifications to better accommodate vegetable oil fuels. These recommendations include addition of fuel heaters and modified injectors.

Engine performance and durability test results encourage the further testing of fuels:

- o containing higher concentrations of high oleic oils
- o formulated as thermodynamically stable nonionic microemulsions
- o containing methanol in the microemulsion
- o formulated as ionic microemulsions.

Fuels of greater oxidative stability need to be developed.

Several investigators still report data for distillation at atmospheric pressure of vegetable oils and fatty acid methyl esters. The temperatures at which those chemicals boil, at ambient pressure, are greater than their decomposition temperatures; consequently, the distillation curves reported are decomposition curves. Those lipid materials may be distilled at greatly reduced pressure in conventional vacuum apparatus or in molecular stills.

The thermodynamic properties of the ester, vegetable oil, and hybrid fuels need to be determined. And the combustion kinetics and flame characteristics should be established for the vegetable oil fuel constituents.

Additive packages need to be developed to improve fuel performance. Perhaps, these additives should address both the fuel and crankcase shortcomings identified with the alternate fuels. Additional lube oil and engine wear information should be obtained. Emissions data are required for successful alternative fuel as they are identified. Naturally, long-term endurance tests of the manufacturers' specifications will need to be conducted on some of the most promising fuels.

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